Building Habitats on Moon/Mars using In Situ Resources with No/Lo Earth Dependence

Supported by Rationale, Practicality and Demonstration

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Abstract

Habitat building on moon has been a long sought-after human dream. The six successful Apollo missions became the impetus of renewed interest and fueled the passion for the conquest of moon during the past 50 or so years. However, moon (and other planets) are quite different from earth, in terms of composition and environment. The notion of existence of any form of life on them at any point of time up to now is only speculative. Hence, it is neither easy nor practical to imagine that transitioning to moon will simply be an extension of what we have and expect on earth. In this context, the availability of relevant materials and resources on a planets themselves offers the possibility of their utilization in generating propellants and other infrastructure that could assist long-term human endeavors, life support and eventual habitation.

The in situ resource utilization (ISRU) - either in the form of raw materials or as the finished structural and/or functional components - would ease the logistic burden, both on the international space station (ISS) and the earth. Thus, the benefits of ISRU are far greater for the manned space missions than for their robotic counterparts, simply because they are larger in scope and scale.

From system design point of view Johnson Space Center (Houston, TX), Kennedy Space Center (Cape Canaveral, FL), NASA Langley Research Center (Hampton, VA) and Glenn Research Center (Cleveland, OH) have made tremendous in-roads on ISRU-related aspects. This presentation is an attempt to forge a collaboration with Colorado School of Mines faculty to explore what else could be done with the resources available on the moon and Mars to help develop an infrastructure that would one day make these extraterrestrial bodies habitable.

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Ground reality: Moon *vs.* Mars

- Moon is a body of no atmosphere, high vacuum: only traces of solar wind gases, that escape quickly into space. No natural heat exchange medium on its surface.
- Size of moon is ~1/4th and its weight ~1/100th of Earth.
- *g*: only 1/6th of that on earth – makes lifting and supporting of materials less of a problem.
- A day on moon = 27.32 Earth days (or 655.72 h); each day and night on moon is about 328 h long (*vs.* 12 h on earth).
- Lunar surface is bathed in sunlight during its daytime, without uncertainties from cloud coverage.
- Sunlight available full-time in the orbit and along the rim; bases at polar locations also utilize solar energy full-time.
- Surface temperatures range from about -170°C in the night to as high as +120°C in direct sunlight; the average temperature on moon is -30°C.

- Martian atmosphere composed of CO_2 (~95.9%), N_2 (2%), Ar (1.9%), O_2 (0.14%) and CO (0.06%); remainder, traces of CH_4 and H_2O. Martian atm. pressure ~ 1/100th of earth's (~7 Torr).
- Mars is ~1/2 the size of Earth and weighs ~1/10th of Earth.
- *g*: only 1/3rd of that on earth – makes lifting and supporting of materials less of a problem.
- Average day on Mars almost same as the Earth day (~ 24h 40 min. *vs.* 24 h); one Mars year = 687 days (*vs.* 365 Earth days).
- Mars receives only ~45% of the sunlight compared to what Earth does.
- Temperature ranges between a low of -143°C during the winter at the poles to a high of 35°C during summer and midday at the equator.
- Average temperature of Mars surface is -46°C.

- The premise and logic of this presentation is based primarily on some parallel work – ours and others' – (though STRICTLY not from ISRU angle, per se):

a) conversion of CO_2 (a byproduct of fossil fuel combustion and a potent GHG on Earth) into C, CO and O_2

b) conversion of H_2O (also a byproduct of fossil fuel combustion and a potent GHG on Earth) into H_2 and O_2

c) beneficiation of steel industry's 'mill-scale' waste – iron oxide (Fe_3O_4)

d) utilization of CO_2 as a feedstock for making methanol – an important industrial chemical

How does this relate to the effort towards sustained human presence on Moon or Mars?

- CO_2: the most dominant constituent of Mars environment
- H_2O: determinately scarce commodity on Mars (frozen ice and hydrated minerals)
  - Both non-existent on Moon
- Iron oxide found in both lunar and Martian regolith

Premise and Disclaimer (2)

- Most intensely pursued pathway by ISRU proponents: Hi-T electrolysis of CO_2 and H_2O to obtain O_2 (and CO & H_2)

- Generate CH_4 by Sabatier reaction between CO_2 and H_2 or CO and H_2: JSC/KSC/GRC lead players

  ➢ Caveat:

  - calls for separation/compression/liquefaction/storage: adds to the complexity
  - needs pumps, additional i

  Focus of this presentation: ISR exploitation & NOT the system or architecture optimization!

  ➢ More practical options:

  - PEMFC running on humidified H_2 stream - a proven lo-temp hi-efficiency system
  - ideal power source for humans occupying the Lunar/Martian habitats.
  - why not make F-T liquid(s) from H_2 and CO precursors instead?

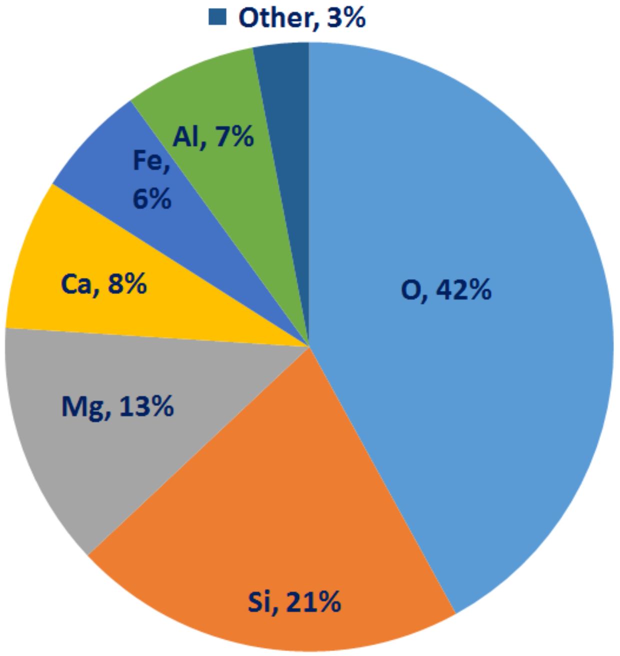
- Transform abundant minerals efficiently into *other* value-added products – beside propellants
  - Martian/lunar mineral composition quite similar to those found on earth!
  - minerals, soil and dust: adequate precursors for building habitat infrastructure

- Use renewable energy (mostly solar) as heat and electricity source

Average composition (mass%) of the lunar surface*

O (43.4%)
Si (20.3%)
Mg (19.3%)
Fe (10.6%)
Ca (3.2%)
Al (3.2%)
Cr (0.42%)
Ti (0.18%)
Mn (0.12%)

Composition (mass%) of lunar regolith*



Looks like plenty of oxygen: not free though; all bound!

Planetary and Space Science 74 (2012) 49–56

The production of oxygen and metal from lunar regolith

Carsten Schwandt [a,b,*], James A. Hamilton [b], Derek J. Fray [a], Ian A. Crawford [c]

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[b] Green Metals Ltd., London, UK
[c] Department of Earth and Planetary Sciences, Birkbeck College, University of London, London, UK

Table 1
Chemical compositions of lunar simulants JSC-1 (NASA, 2005) and NU LHT (NASA, 2008). Composition ranges are given for JSC-1 to reflect the slightly varying specifications for this material.

Oxide	JSC-1, % by mass	NU LHT, % by mass
SiO_2	46–49	46.7
Al_2O_3	14.5–15.5	24.4
CaO	10–11	13.6
MgO	8.5–9.5	7.9
Na_2O	2.5–3	1.26
K_2O	0.75–0.85	0.08
TiO_2	1–2	0.41
MnO	0.15–0.20	0.07
FeO	3–4	–
Fe_2O_3	7–7.5	4.16
Cr_2O_3	0.02–0.06	–
P_2O_5	0.6–0.7	0.15

- Abundant in the lunar minerals, soil and dust: SiO_2, MgO, CaO, FeO_x (FeO, Fe_2O_3), Al_2O_3,
  Present in low mass fraction: TiO_2, MnO_x, CrO_x, (Na_2O, K_2O, P_2O_5)
- NO FREE O_2 and NO hydrated minerals: Very dry; no moisture (liquid H_2O or solid ice)

*G.A. Landis, *Acta Astronautica*, **60** (2007) 906-915.

LHT: Lunar High Titanium mare soils

Moon's minerology

- Abundant in the lunar minerals, soil and dust: SiO_2, MgO, CaO, FeO_x (FeO, Fe_2O_3), Al_2O_3
  Present in low weight fraction: {TiO_2, MnO_x, CrO_x, (Na_2O, K_2O, P_2O_5)}

Approximate chemical state of the lunar minerals:
Olivine $(Mg,Fe)_2SiO_4$ - rich in Mg, Fe, Si and O
Anorthite $CaAl_2Si_2O_8$ - rich in Ca, Al, Si and O
Pyroxene $(Ca,Na)(Mg,Fe,Al)(Al,Si)_2O_6$ - rich in Mg, Fe, Al, Si and O, w/ small amounts of Na and K
Ilmenite $FeTiO_3$ - rich in Fe, Ti and O

↓

Natural resource for:
(a) Structural metals (Al, Mg, Ti and/or Fe)
(b) Value-added structural and functional glass & ceramics: relevant to habitat infrastructure

Some *earthly* applications

Olivine Mg_2SiO_4-Fe_2SiO_4 (olive-green, hence the name): combination of forsterite (Mg_2SiO_4) & fayalite (Fe_2SiO_4)

- Gemstone 'peridot': dark olive-green to bright lime-green (depending on the fayalite content in the mineral).

- Mostly used in metallurgical processes as a slag conditioner:

  Removes impurities from steel and forms slag in blast furnaces.
- Used as a refractory material (refractory bricks and casting mold).

yet unexplored for space!

Anorthite/Anorthosite (plagioclase feldspar) $CaAl_2Si_2O_8$

- Natural anorthite is lightweight (sp. gravity ~2.76) and has no commercial use.
- Synthetic anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS2) is used in cement and ceramic industry.
- Due to high melting point (1550°C), used in composites for high-temperature applications.
- Cal-Sil [Ca_2SiO_4 ($2CaO \cdot SiO_2$)] is a safe, low-cost structural alternative to asbestos used in bricks, roof tiles, roads, insulation, cement-compatible spacers, etc.

yet unexplored for space!

Pyroxene $(Ca,Na)(Mg,Fe,Al)(Al,Si)_2O_6$

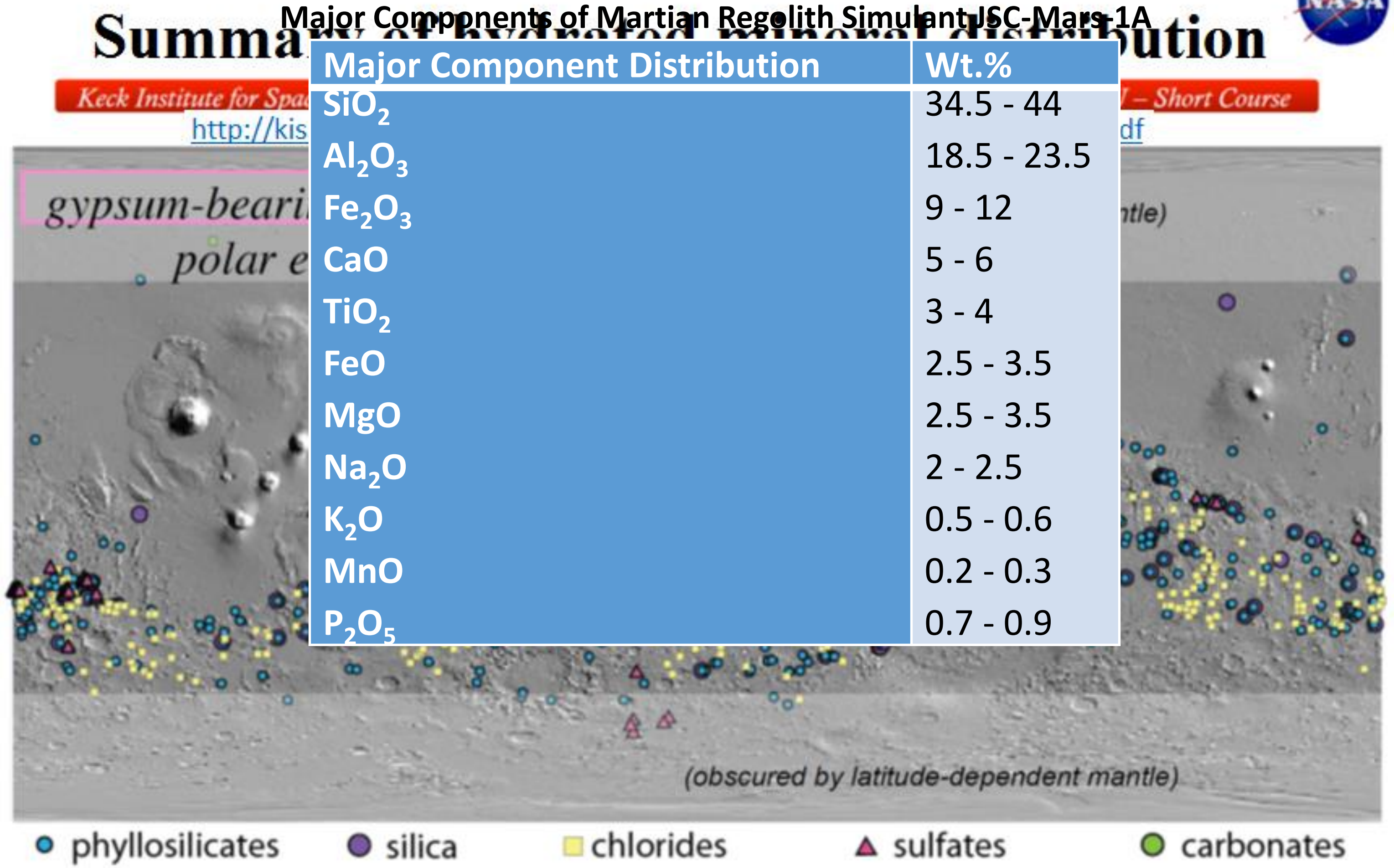
- Commonly occurs with olivine, plagioclase, magnetite and other minerals.
- Of little economic value at its own, but in coexistence with others, may become valuable construction material. **yet unexplored for space!**

Ilmenite $FeTiO_3$

- A good source of titanium metal: Ti used in steel strengthening & as electrode in welding and electrochemistry.
- Also used for making titania (TiO_2) - a source material for abrasives.
- TiO_2 - a precursor for white reflective pigment in paints, paper, plastic, rubber, etc.
- An efficient oxygen carrier for chemical looping combustion.
- Potential catalyst and/or catalyst support?

yet unexplored for space!

Composition of Mars Regolith



Major Components of Martian Regolith Simulant JSC-Mars-1A

Major Component Distribution	Wt.%
SiO_2	34.5 - 44
Al_2O_3	18.5 - 23.5
Fe_2O_3	9 - 12
CaO	5 - 6
TiO_2	3 - 4
FeO	2.5 - 3.5
MgO	2.5 - 3.5
Na_2O	2 - 2.5
K_2O	0.5 - 0.6
MnO	0.2 - 0.3
P_2O_5	0.7 - 0.9

- Abundant … FeO_x (Fe_2O_3, Fe_3O_4)
- Present in … MgO, Na_2O}
- Abundant in Martian environment: CO_2
- Abundant in Martian minerals: H_2O (as water of hydration of sulfates, carbonates, chlorides, silica and phyllosilicates)

Sustaining Human Presence on Moon/Mars would require:

- Understanding the system and technology needs for a **sustained human presence** on the Moon/Mars surface
- Maximizing the utilization of SiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, TiO_2, CaO, MgO, H_2O and CO_2 at minimum energy usage/penalty.

- For sustained human presence, water is the most fundamental enabling resource to support human life
- By continuing to expand manufacturing on Moon/Mars, it is possible to minimize the cost and reduce Earth dependence

The true meaning of 'have' and 'have not's!

Exploiting abundance

Managing scarcity

Gravity on moon is 1/6th and on Mars 1/3rd of earth!

*From Robert Moses (NASA Langley)'s presentation at the AIAA Space 2015 Conference, Pasadena, CA (8/31-9/2, 2015)

Sustaining Human Presence on Moon/Mars would require:

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Goal must be to produce:

1. Propellants (oxygen and fuel)
2. Metals and structural alloys (Fe, ferrosilicon, Al, Ti, etc.)
3. Structural/building materials (cement, concrete, bricks, fillers)
4. Radiation-shields for personnel and habitats (glass and ceramics)
5. Electronic/magnetic components (motors, sensors and actuators)
6. Electroceramics (including catalysts)

Envisaged usage of SiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, {CaO, MgO, TiO_2}, H_2O and CO_2 on **Mars**

Material(s)	Application(s)
SiO_2, Al_2O_3, FeO_x (with/without alkali metal & phosphate microconstituent incorporation)	Aluminosilicate/ferro aluminosilicate as (a) structural ceramics (b) reinforcement fiber glass (c) radiation-shielding glass (d) habitat windows
MgO, CaO (calcined dolomite)	Flux in iron and steel making
CaO, SiO_2 (calcium silicate)	**Cal-Sil** - a low cost structural material (safe alternative to **asbestos**) used in bricks, roof tiles, roads, insulation, etc. Ca_2SiO_4 ($2CaO.SiO_2$) a cement-compatible spacer
MgO, SiO_2 (magnesium silicate)	Steatite - a low cost material with • high electrical resistance at high temperatures • good mechanical strength • very low dielectric loss factor. • Ideal for high frequency, low loss, and high voltage insulation.
FeO_x, TiO_2 (iron titanate, ilmenite)	Pure and doped $FeTiO_3$, solid-state oxygen carrier and fuel oxidation catalyst
CaO, TiO_2 (calcium titanate)	In doped form, $CaTiO_3$ is a solid-state oxygen carrier and fuel oxidation catalyst
MgO, TiO_2 (magnesium titanate)	$MgTiO_3$ useful as low dielectric support material for making on-chip capacitors, high frequency capacitors and temperature compensating capacitors
Fe_2O_3, Fe_3O_4, H_2O and CO_2	Precursors to O_2 generation and fuel manufacturing
Fe_2O_3, Fe_3O_4, H_2O and CO_2	Precursors for the fabrication of ceramic permanent magnet (motors, actuators)

Goals:

Maximized ISRU
Lo earth-dependence
Lo energy usage
Simple processing
High-end products

Proposed approach to building habitat: maximize ISRU (MISRU)

MOON

An intermediate conduit as a processing, storage and manufacturing hub in LEO

ISS

Critical ingredient/ component source

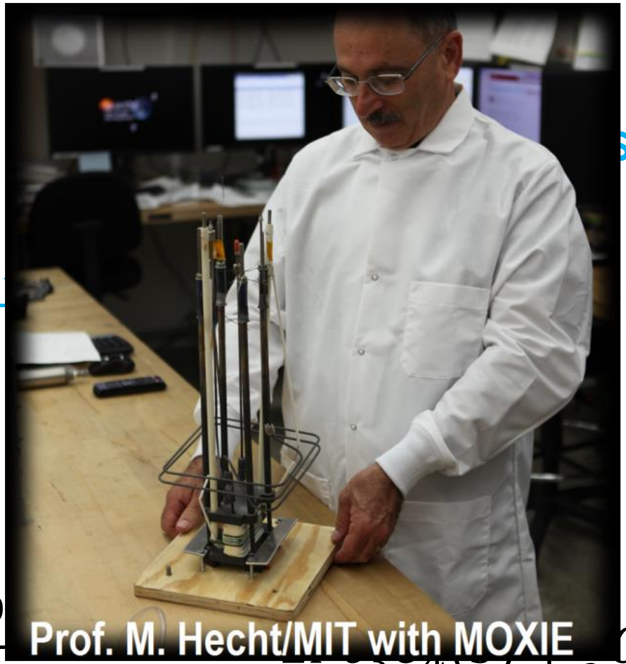
EARTH

MARS

Oxygen production

OPTION I: Solid Oxide Electrolysis of CO_2 and/or H_2O (**MOXIE**)*

$$CO_2(g) \xrightarrow{800℃,\, current} CO\ (g) + \tfrac{1}{2}O_2(g) \qquad || \qquad H_2O(g) \xrightarrow{800℃,\, current} H_2(g) + \tfrac{1}{2}O_2(g)$$



Power: 300 W
Dimension: 9.4 x 9.4 x 12.2 in. (23.9 x 23.9 x 30.9 cm)
Production rate: ~10 g/h (0.022 lb/h) oxygen from Martian carbon dioxide
Time to produce: ~ 2 h
Operating temperature: 800°C/1472°F

OPTION II: … s o…

$CO_2(g) \xrightarrow{\sim 750℃, …}$ …) … (g)

OPTION III: … O…

$3Fe_2O_3(s) \xrightarrow{850…} 2Fe_3O_4(s) + \frac{1}{2}O_2(g)$ *Mars*

$FeTiO_3(s) \xrightarrow{\geq 900℃} Fe\ (s) + TiO_2(s) + \frac{1}{2}O_2(g)$ *Moon*

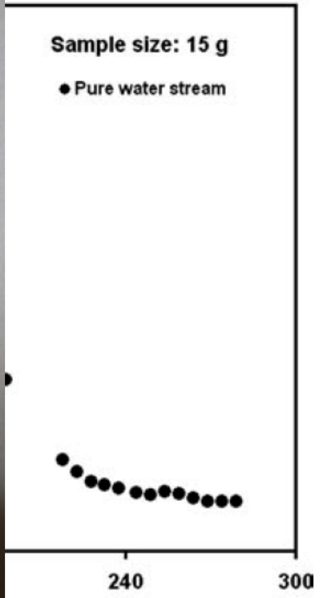
*: Mars **OX**ygen **I**n-situ resource utilization **E**xperiment

Fuel production

OPTION I: via simultaneous resource utilization

$$(a)\ 2Fe_3O_4(s) + CO_2(g) \xrightarrow{\geq 580^\circ C, 1\ atm.} 3Fe_2O_3(s) + CO(g)$$

$$(b)\ 2Fe_3O_4(s) + H_2O\ (g) \xrightarrow{\geq 580^\circ C,\ 1\ atm.} 3Fe_2O_3(s) + H_2(g)$$



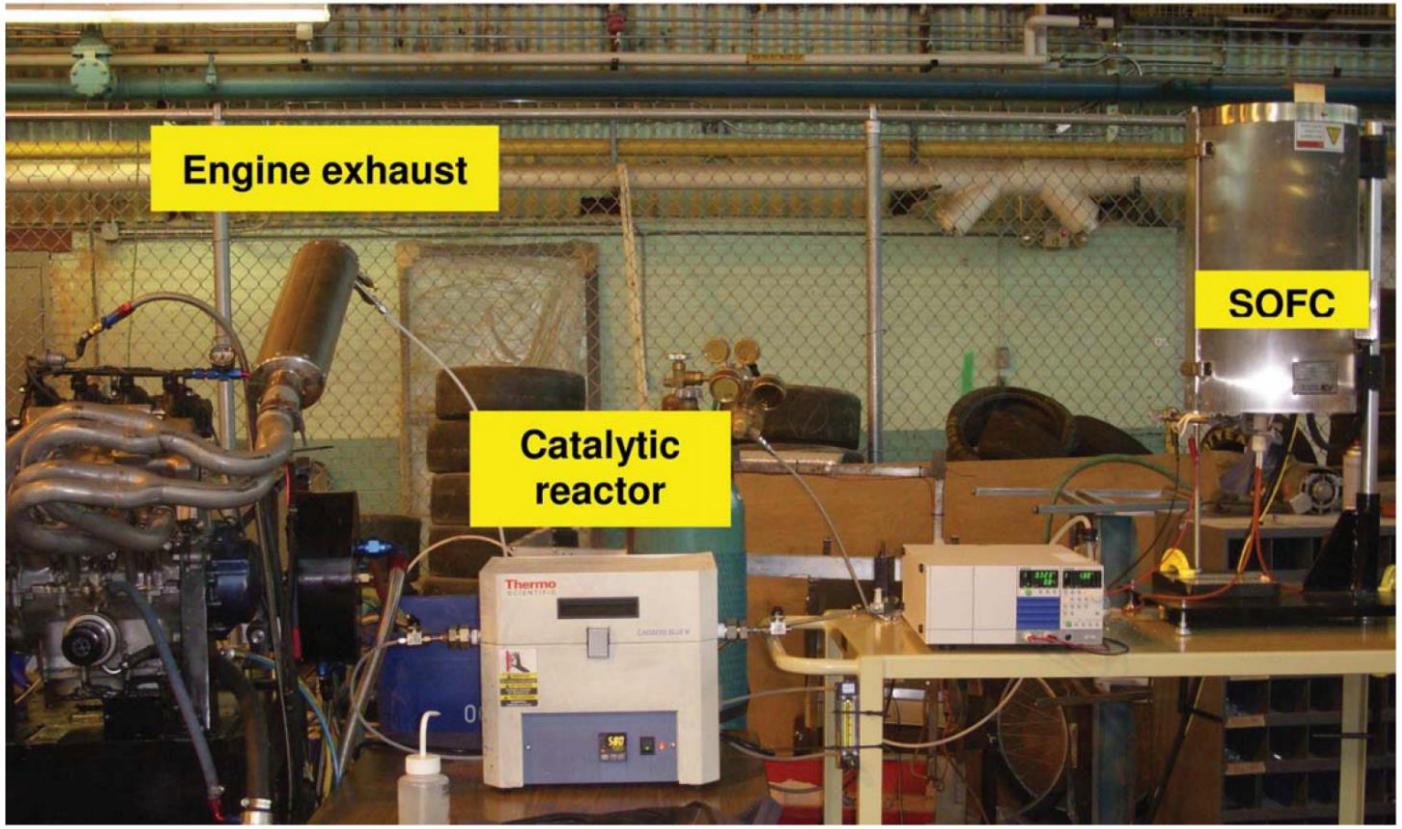
Time dependence of CO generation from CO_2 with Fe_3O_4.

As-received (L) and ball-milled (R) steel industry mill-scale waste

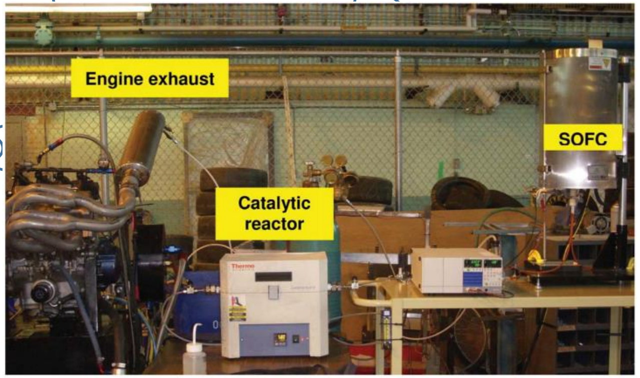
Evidence of H_2 generation from pure water stream in contact with the magnetite.

Fuel production

$$(c)\ 2Fe_3O_4(s) + \overbrace{CO_2(g) + H_2O\ (g)} \xrightarrow{\geq 580℃, 1\ atm.} 3Fe_2O_3(s) + \overbrace{[CO + H_2]}(g)$$



Experimental set up for the concept validation using engine exhaust feed.



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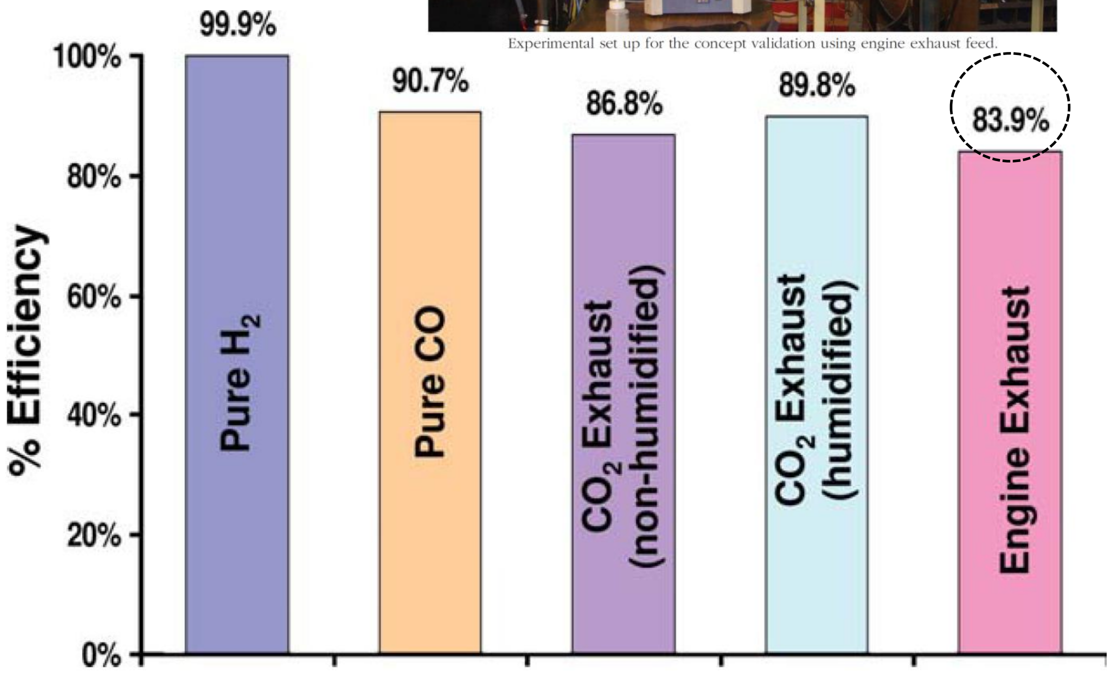


Comparison of the efficiency of a single-button fuel cell at 650°C on different feeds; the efficiency is defined as the ratio of $OCV_{(GHG\ fuel)}$ to $OCV_{(H_2)}$.

Fuel production

OPTION II: Other fuel-making scenarios with Martian precursors

$Sabatier\ reaction$: $4H_2(s) + CO_2(g) \xrightarrow{catalytst} CH_4(g) + 2H_2O(g)\ ;\ \Delta H_{298K} = -252.9\ kJ\ mol^{-1}, \Delta G_{298K} = -130.8\ kJ\ mol^{-1}$

$RWGS\ reaction$: $CO_2(g) + H_2(g) \xrightarrow{catalyst} CO(g) + H_2O(g)\ ;\Delta H_{298K} = -41.2\ kJ\ mol^{-1}$

$F - T\ reaction$: $n\ CO\ (g) + (2n+1)H_2(g) \xrightarrow{catalyst/150℃,\ 5-25\ atm.} C_nH_{2n+2}(s) + nH_2O(g)$

$Olefication:\ CO\ (g) + 2H_2(g) \xrightarrow{Fe_2O_3-based\ catalytst} -CH_2-(g) + H_2O(g)\ ;\Delta H_{R,\,298K} = -166\ kJ\ mol^{-1}$

$Boudouard\ reaction$: $2CO(g) \xrightarrow{catalyst/700-1100℃} CO_2(g) + C(s)^{*}\ \Delta H_{298K} = -171.8\ kJ\ mol^{-1}, \Delta G_{298K} = -165.6\ kJ\ mol^{-1}$

Catalysts????

Mostly Al_2O_3, ZrO_2 or SiO_2-supported TMOs (CuO, ZnO, Cu-Zn, Fe_2O_3, NiO, etc.)
Active components usually not available on Moon or Mars (except perhaps Fe_2O_3)
Must be resourced from earth or made in LEO!

* Solid fuel/reductant; also producible via molten salt electrolysis of CO_2

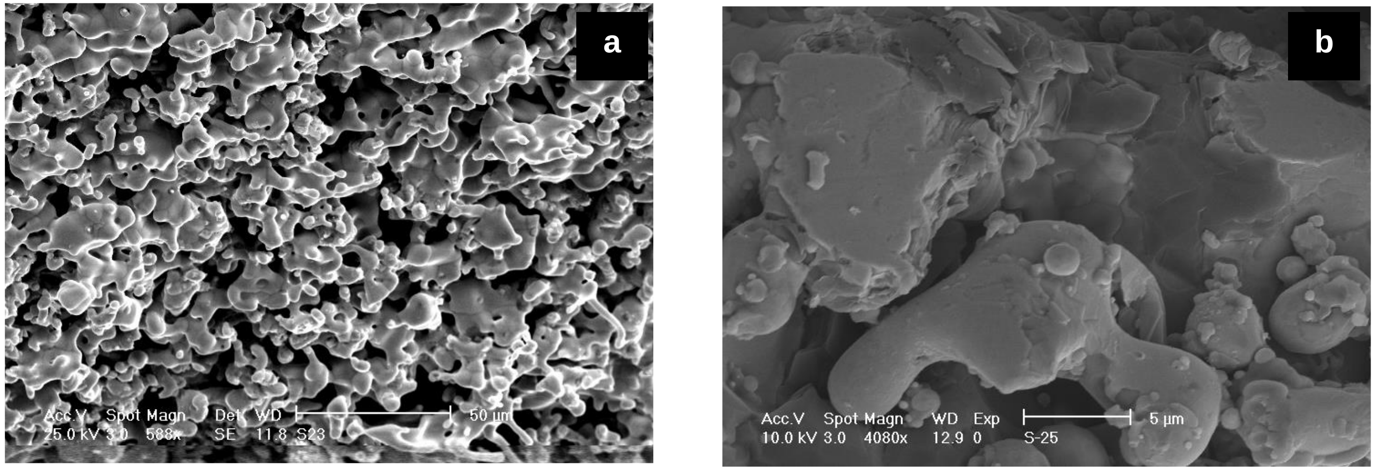
Other Moon/Mars-relevant processes

I: Carbothermic reduction of iron oxide to metallic Fe/C-steel

$$Fe_2O_3(s) + 3C\ (s) \xrightarrow{1000-1100℃} 2Fe\ (s) + 3CO\ (g)$$

(C : oxide ratio > 3)

coarse (macroscale/microscale) Fe agglomerates: lower reactivity



SEM images of carbothermically reduced Midrex (left) and Nucor-Yamato (right) mill-scale waste

II: Fabrication of SiC

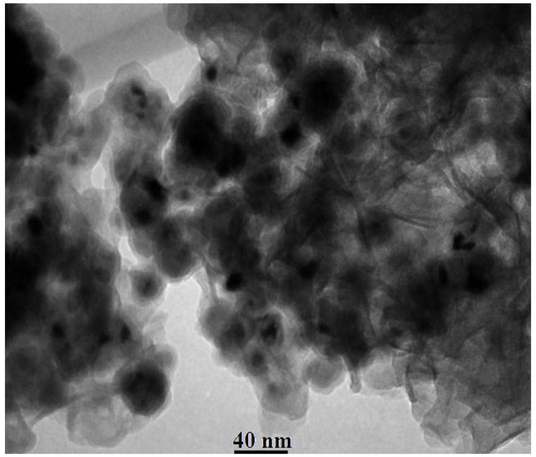
$$SiO_2(s) + 3C\ (s) \xrightarrow{1200-1400℃} [SiC]_C\ (s) + 2CO\ (g)$$

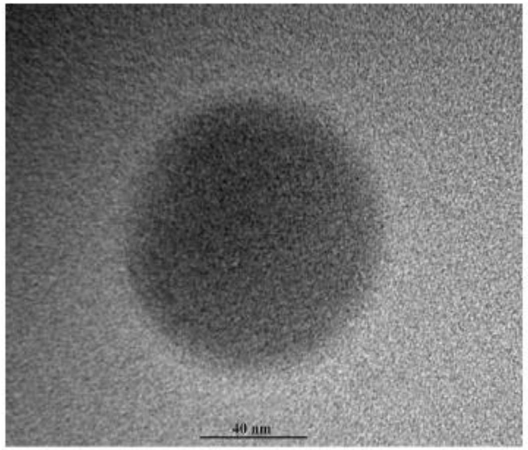
Other Mars-relevant processes ….contd

III: Borohydride reduction of iron oxide to nanoscale Fe

$$Fe^{2+}, Fe^{3+}(acid\ digested\ soln.\ of\ Fe_2O_3, Fe_3O_4) + NaBH_4\ (soln.) \xrightarrow{20℃, 1\ atm.} Fe^0(s) + NaBO_2(soln.)$$

Nanoscale (~40-50 nm) Fe particles at room temperature: highly reactive





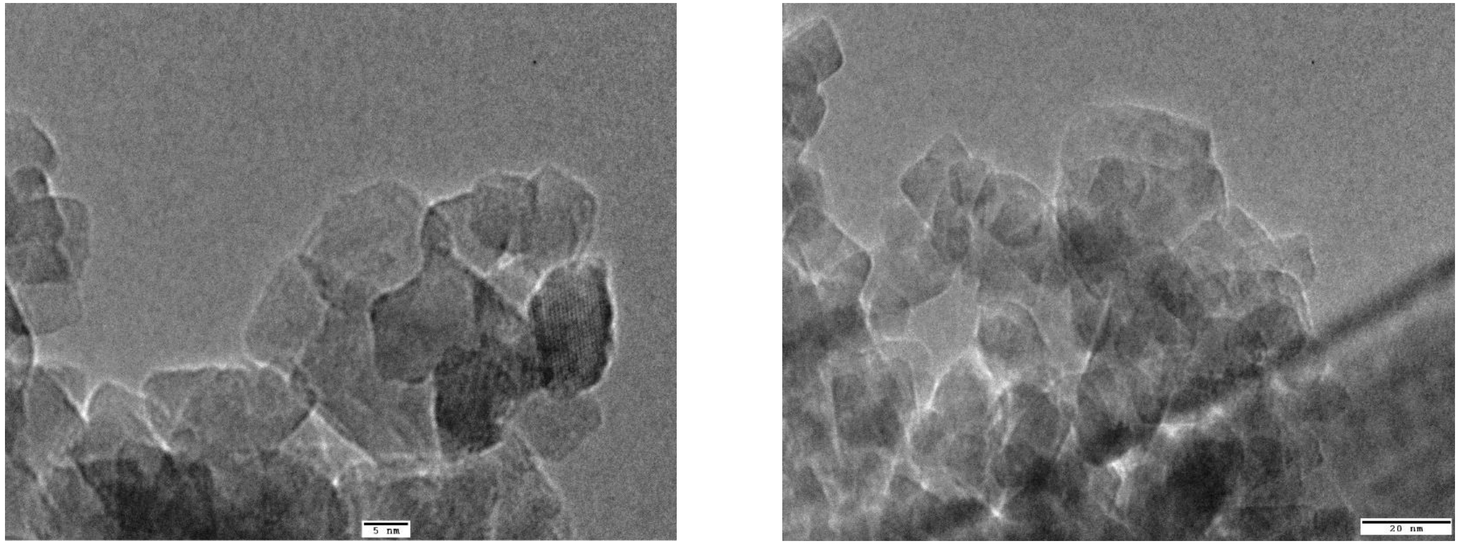
TEM images of elemental Fe obtained at RT via borohydride reduction of acid-digested mill-scale

Other Mars-relevant processes ….contd

IV: Hydrazine reduction of iron oxide to nanoscale Fe

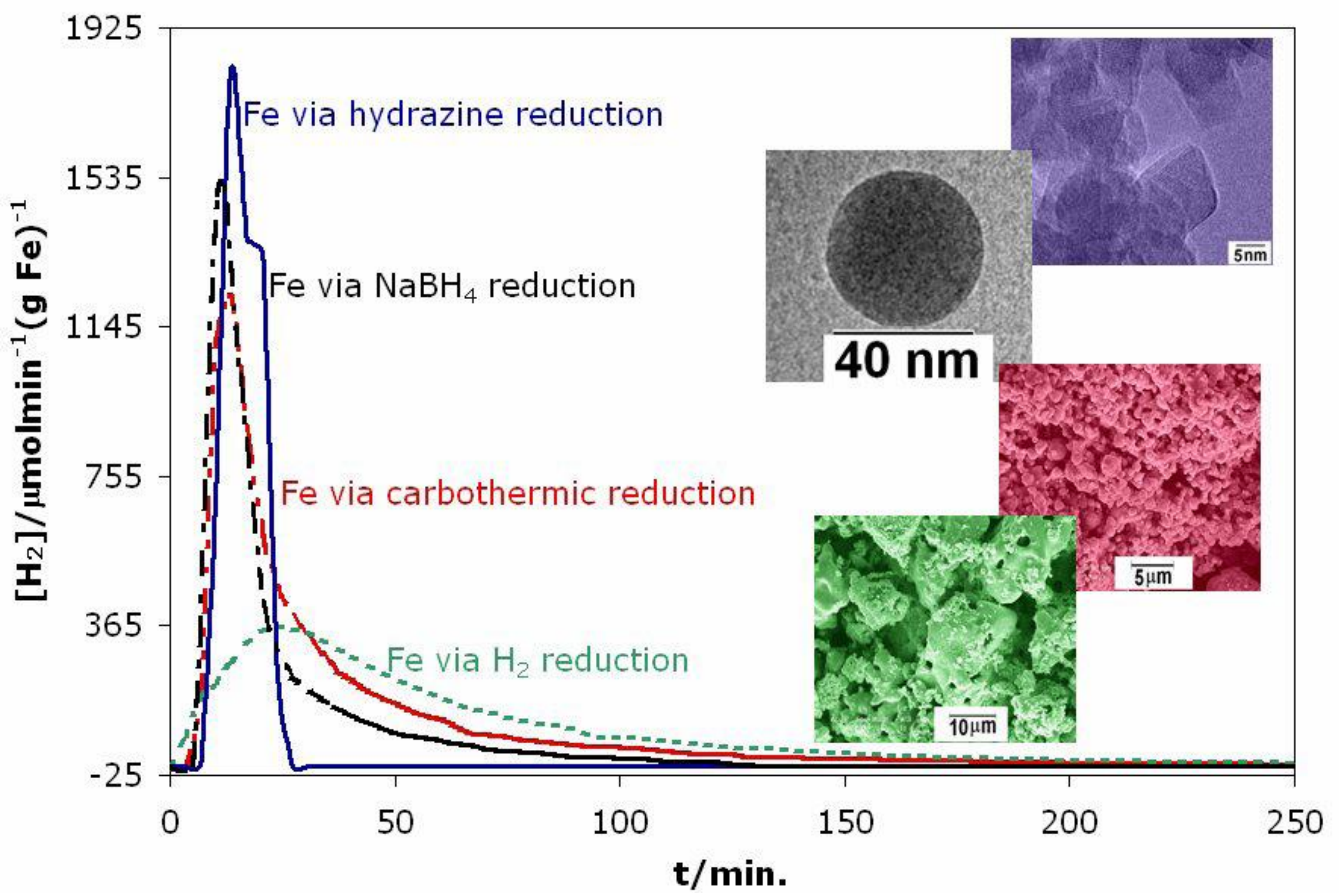
$$Fe^{2+}, Fe^{3+} (acid\ digested\ soln.\ of\ Fe_2O_3, Fe_3O_4) + N_2H_4\ (soln.) \xrightarrow{100℃,\ 5-60\ atm.} Fe^0(s) + H_2O(l) + N_2(g)$$

Nanoscale (~5-20 nm) Fe particles: highly reactive



TEM images of elemental Fe obtained via solvothermal reduction of acid-digested mill-scale by hydrazine at 100°C.

Metal-steam reforming (MSR): $3\ Fe\ (s) + 4H_2O(g) \xrightarrow{\sim 580℃} Fe_3O_4\ (s) + 4H_2(g)$



H_2 yield

↓

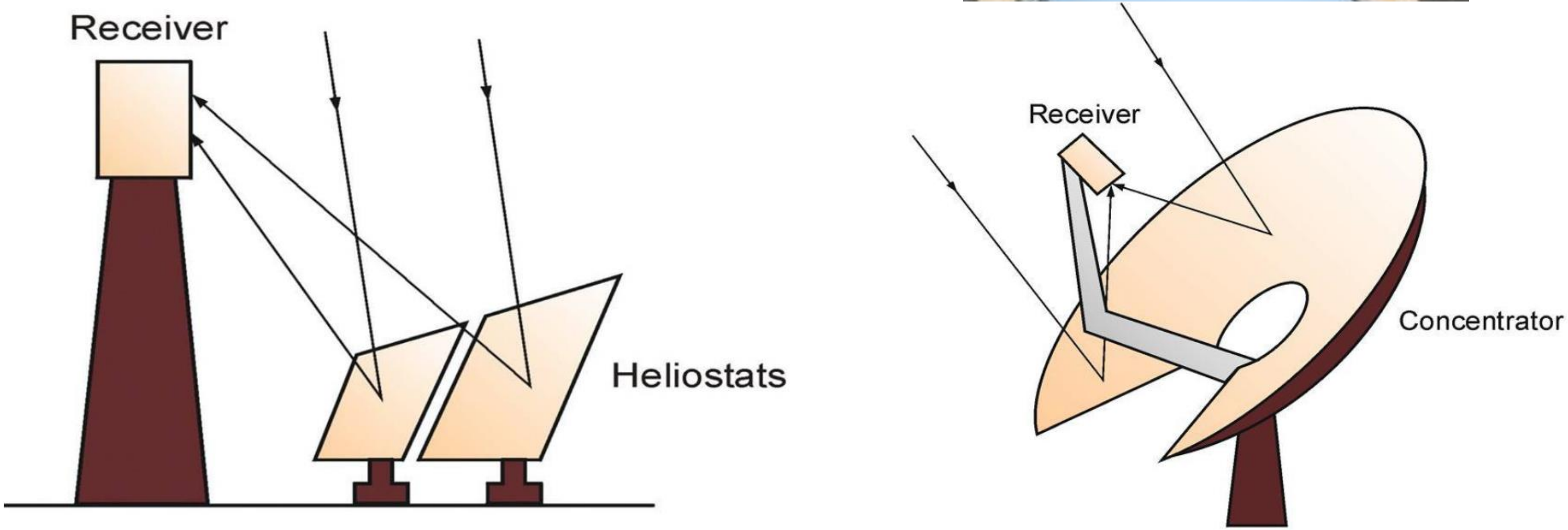
particle size dependent

↓

Fe-making process dependent

Solar H_2-generation via MSR:

$$3\ Fe\ (s) + 4H_2O(g) \xrightarrow{concentrated\ \Delta} Fe_3O_4\ (s) + 4H_2(g)$$



(a) (b)

$s) + H_2(g)$

Schematic of (**a**) a central receiver system and (**b**) a solar dish system

$)(g)$

CO_2 beneficiation via electrolysis in molten carbonate salt

$$M_2O + CO_2 \rightarrow M_2CO_3(2\,M^+, CO_3^{2-})$$

Primary process at the anode

oxygen production: $$2\,CO_3^{2-} \xrightarrow{600-700°C} CO_2 + \frac{1}{2}O_2 + 2\,e^-$$

Primary process at the cathode

metal deposition: $$M^+ + e^- \xrightarrow{600-700°C} M$$

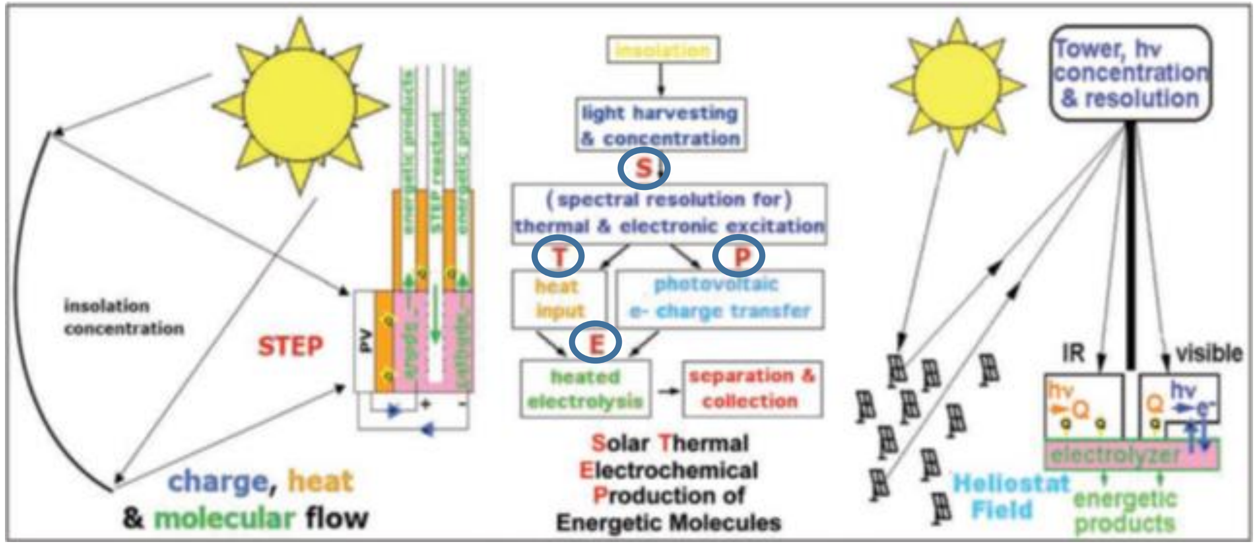
Other processes at the cathode

reduction to CO: $$CO_3^{2-} + 2e^- \xrightarrow{600-700°C} CO + 2O^{2-}$$

reduction to C at lo-temp: $$CO_3^{2-} + 4e^- \xrightarrow{\sim 600°C} C + 3\,O^{2-}$$

metal carbide formation: $$2\,CO_3^{2-} + 10\,e^- \rightarrow C_2^{2-} + 6\,O^{2-}$$

*Heat and Electricity via STEP (**S**olar **T**hermal **E**lectrochemical **P**roduction) Process*



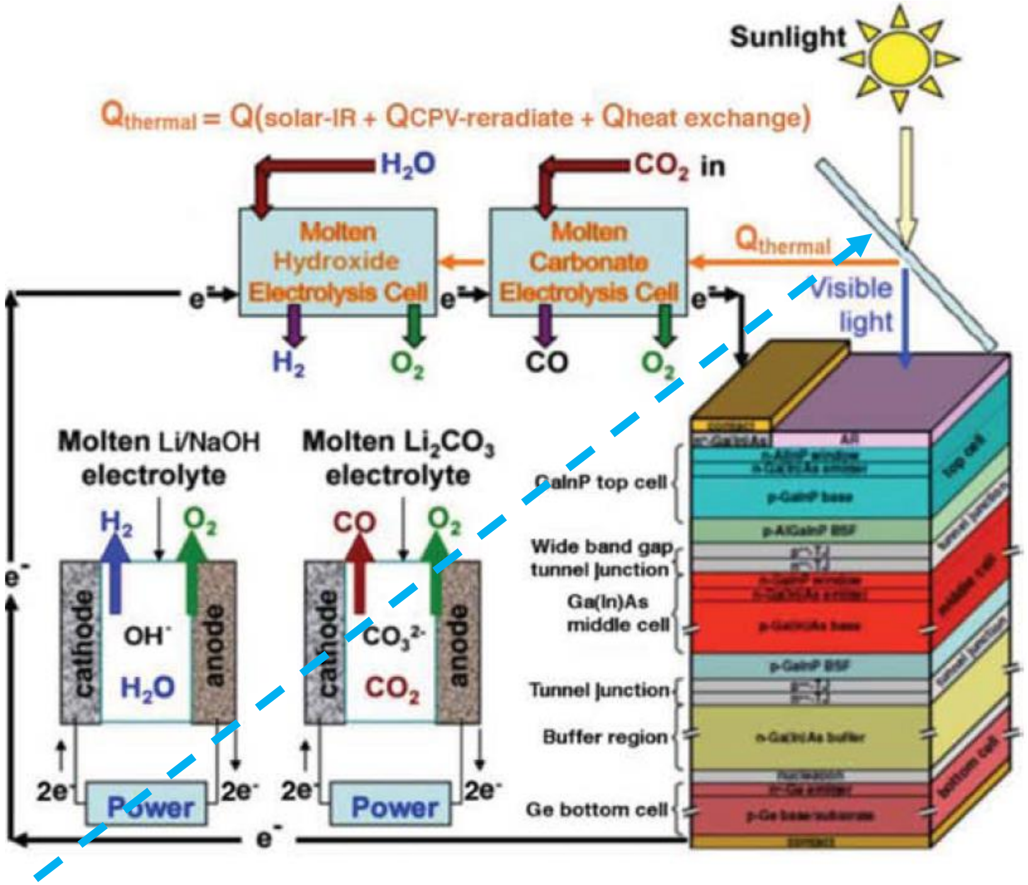
STEP process for the formation of energy-rich species under sunlight.

Black arrow - heat flow

blue - electron flow

green - molecule flow

Insolation: amount of solar radiation reaching a given area



Beam splitter redirects the sub-bandgap sunlight away from PV onto the electrolyzer which is heated by $Q_{thermal}$:

(a) excess solar IR heat (sub-bandgap)

(b) heat re-radiated by CPV preventing it from overheating

(c) heat exchange between the hi-temp products and lo-temp in-flow reactants

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Sungas Instead of Syngas: Efficient Coproduction of CO and H_2 with a Single Beam of Sunlight

*Fang-Fang Li, Jason Lau, and Stuart Licht**

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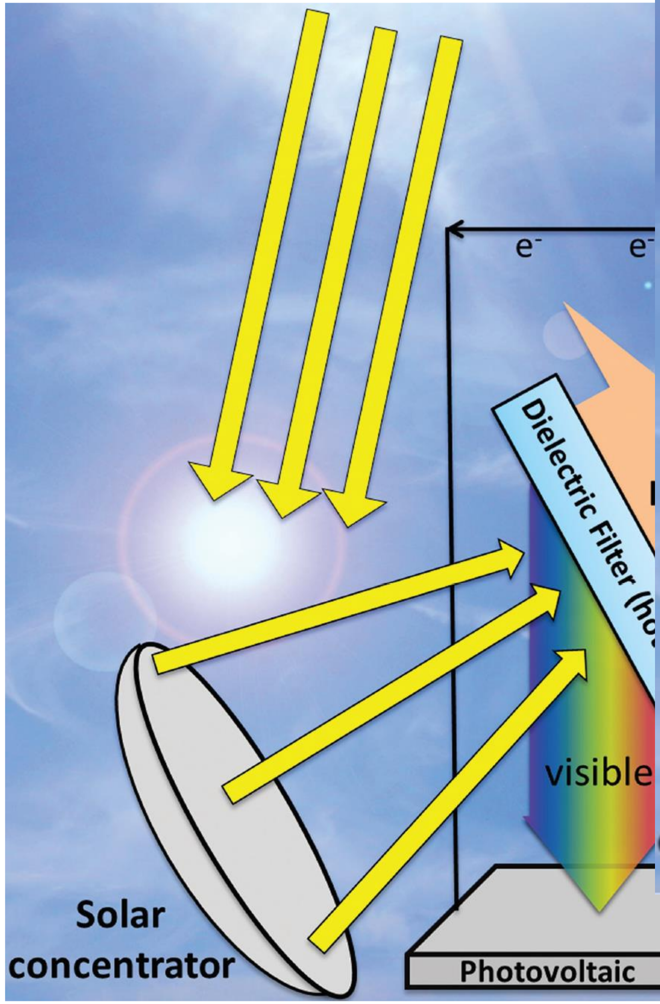
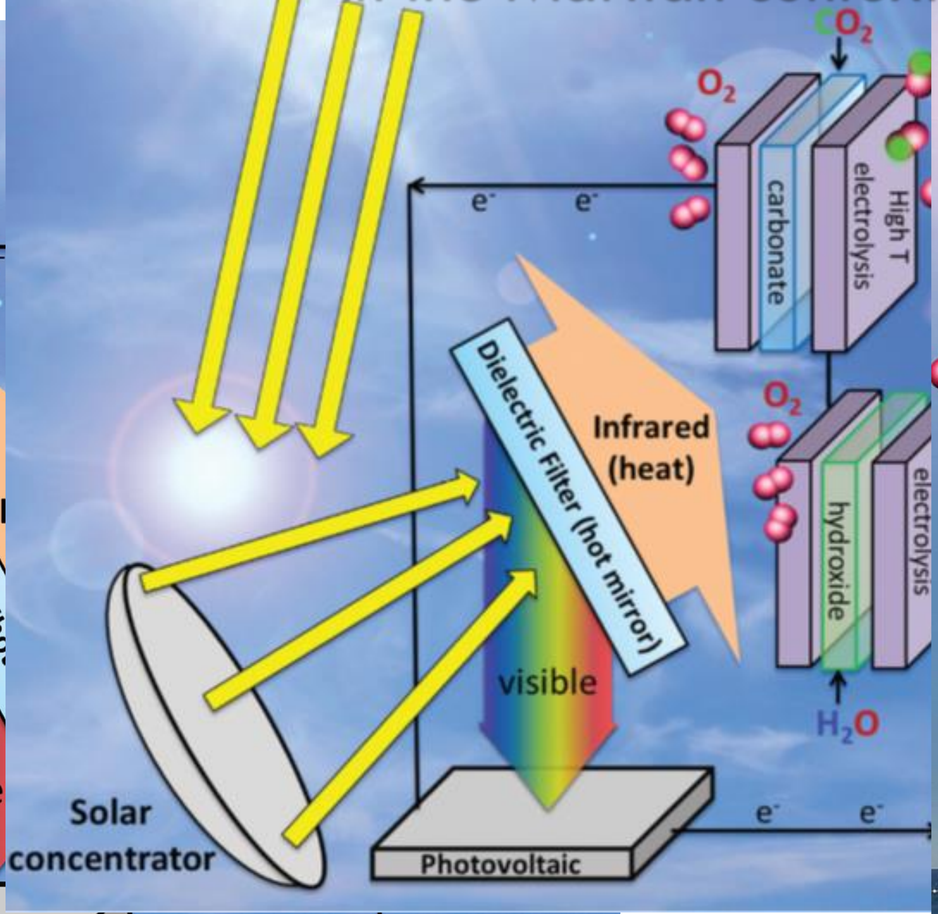
A One-Pot Synthesis of Hydrogen and Carbon Fuels from Water and Carbon Dioxide

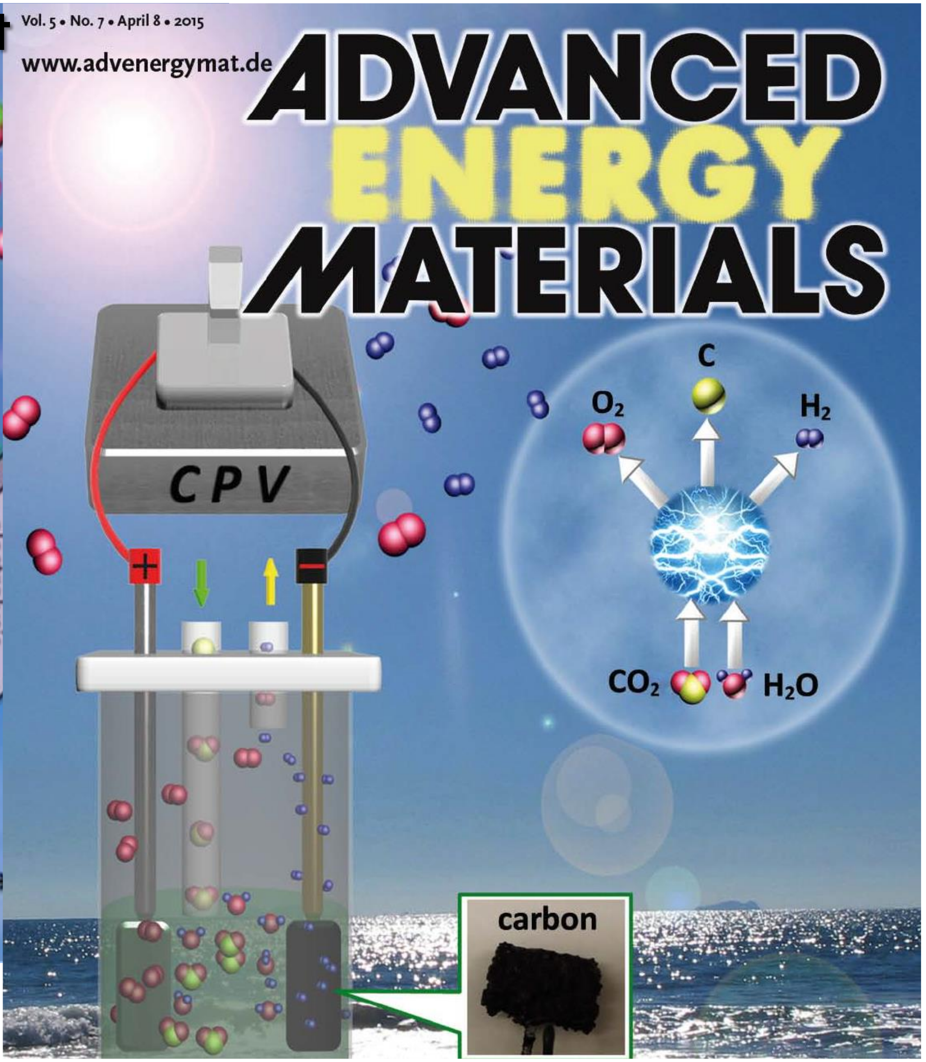
*Fang-Fang Li, Shuzhi Liu, Baochen Cui, Jason Lau, Jessica Stuart, Baohui Wang, and Stuart Licht**

Adv. Energy Mater. **2015**, 5, 1401791

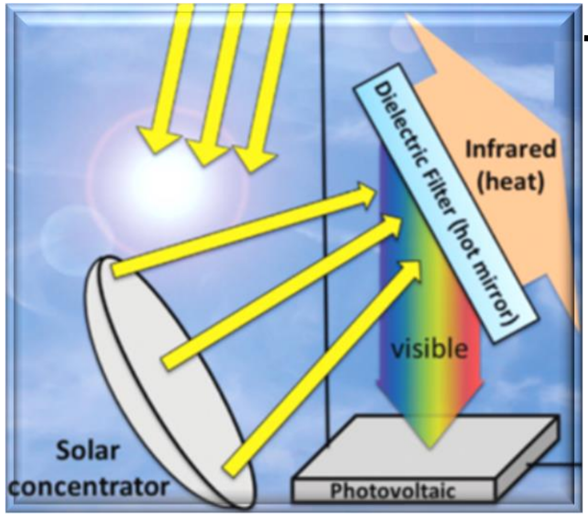
In the Martian context







Ia: Solar generation of propellants (oxygen and fuel) from in-situ '**gaseous**' resources on Mars



CO_2 in an electrolyzer

SOE/MSE of CO_2: "MOXIE"

Pure O_2

CO (+ unutilized CO_2)

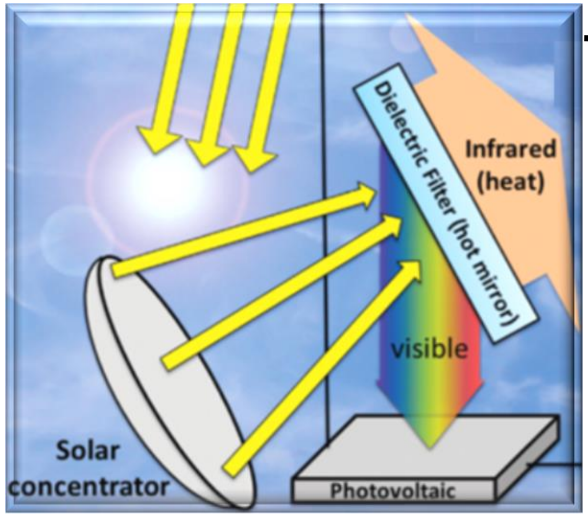
H_2O in an electrolyzer

SOE/MSE of H_2O: "MOXIE"

Pure O_2

H_2 (+ unutilized H_2O)

Ib: Solar generation of propellants (oxygen and fuel) from in-situ ‘**gaseous**’ resources on Mars



SOE/MSE of CO_2

CO_2 in an electrolyzer

Pure O_2

Compress/Store / Utilize

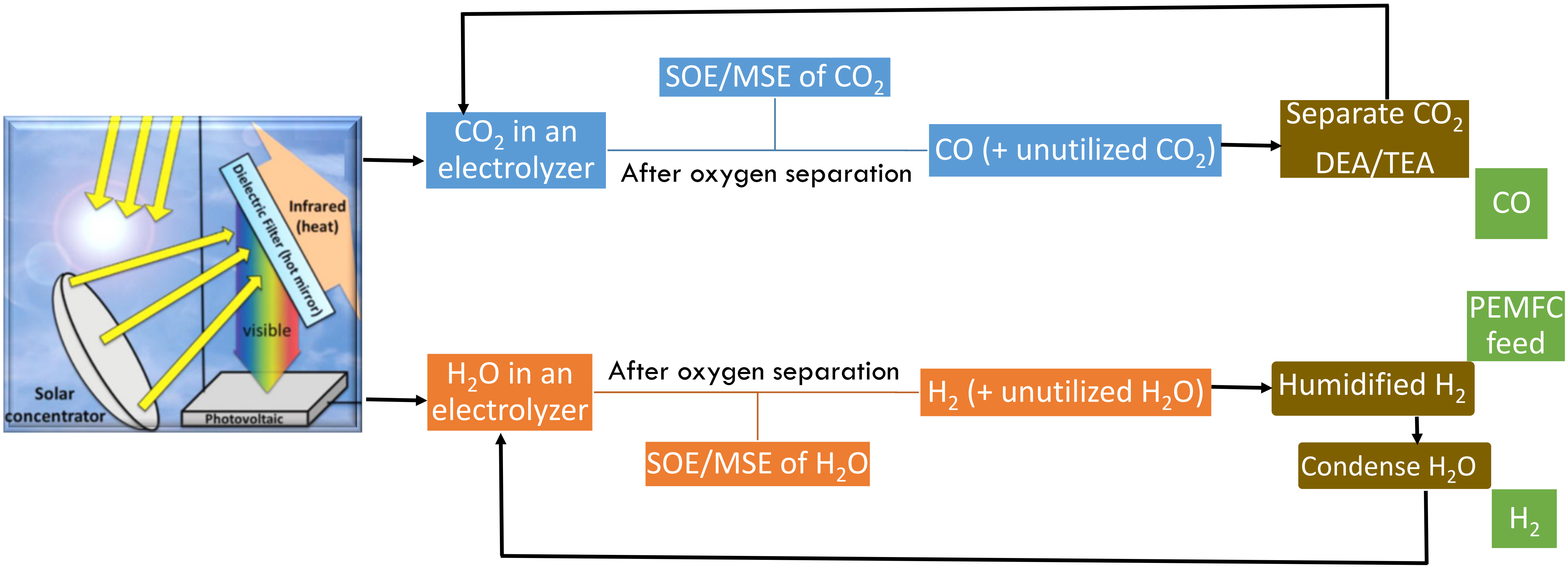
H_2O in an electrolyzer

Pure O_2

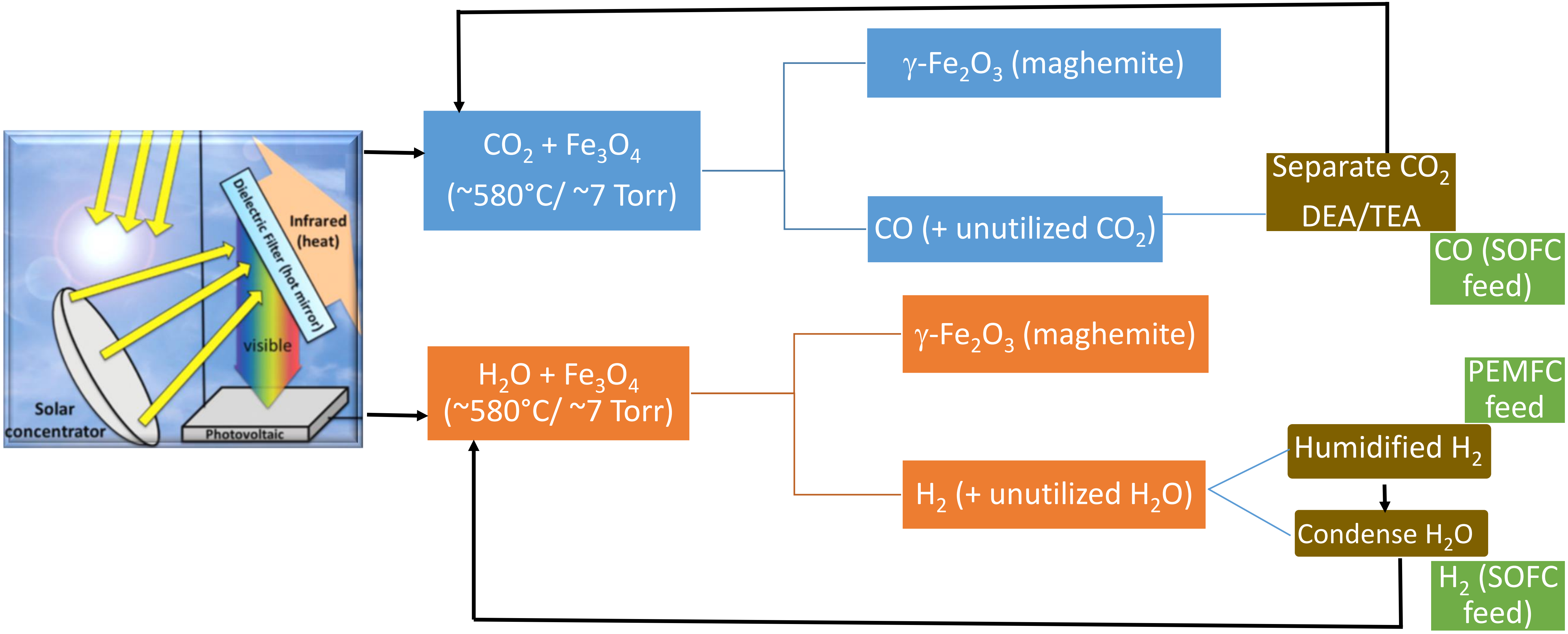
Compress/Store/ Utilize

SOE/MSE of H_2O

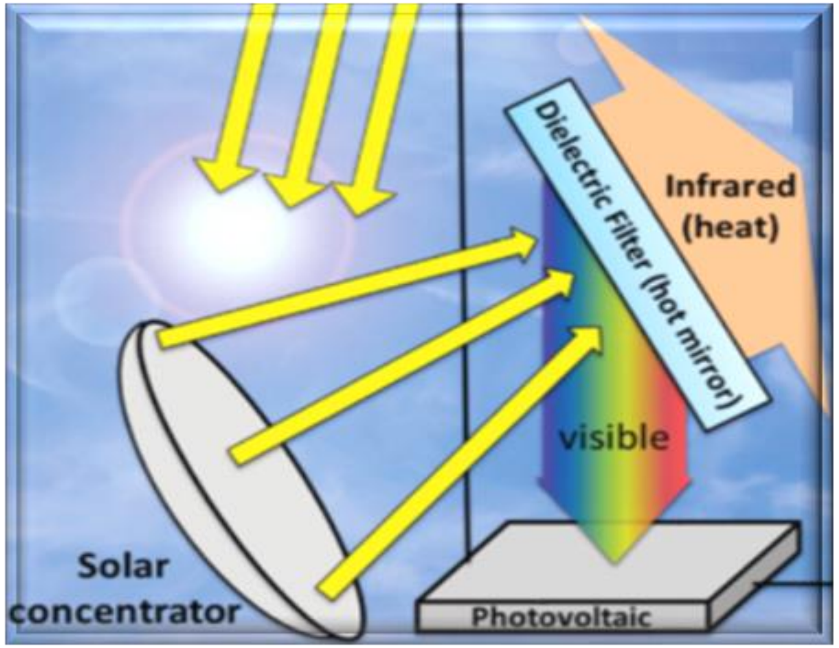
Ic: Solar generation of propellants (oxygen and fuel) from in-situ ‘**gaseous**’ resources on Mars



II: Solar generation of fuel from in-situ '**gaseous + solid**' resources on Mars

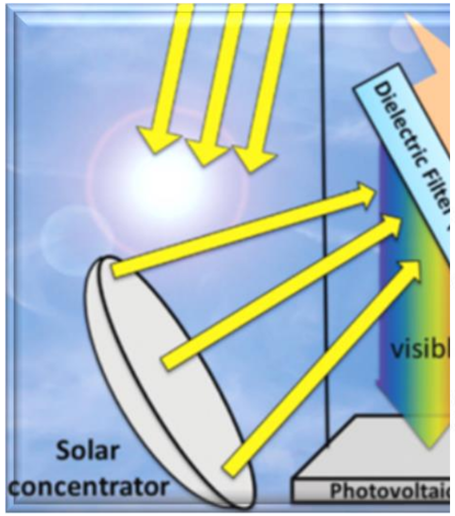


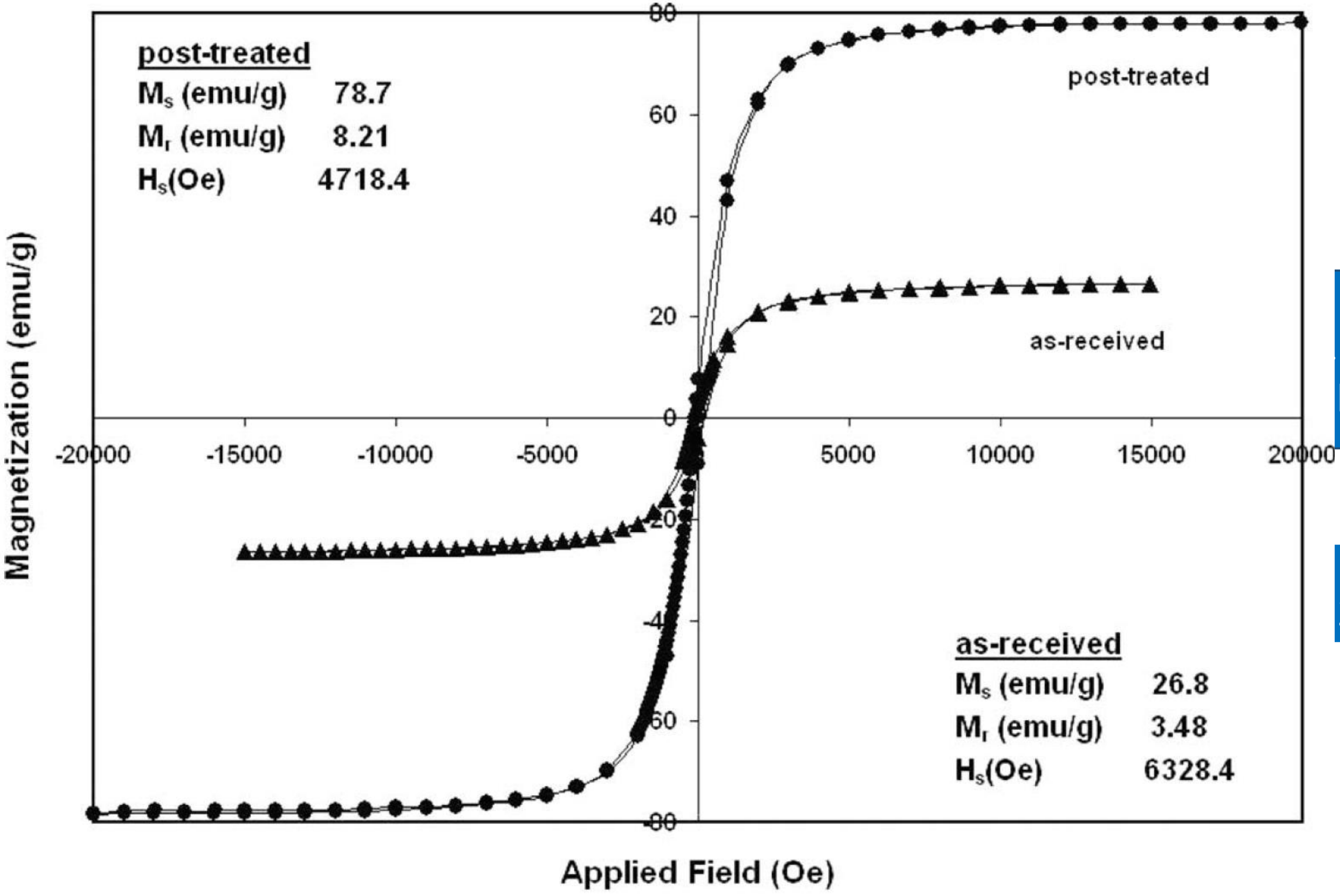
III: Summary of solar fuel options from in-situ '**gaseous + solid**' resources on Mars



$CO + H_2 \rightarrow$ Syngas	$CO + H_2O \rightarrow H_2 + CO_2$ (WGS)	$CO_2 + 4H_2 \rightarrow CH_4 + 2\,H_2O$ (Sabatier)	$CO + 3H_2 \rightarrow CH_4 + H_2O$ (Sabatier)	$CO_2 + H_2 \rightarrow CO + H_2O$ (RWGS)	$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$ (F-T reaction)

Fate of iron oxide precursor in the Martian soil/dust after reaction with Martian CO_2 and/or H_2O





Fe_3O_4 magnetization curve before and after exposure to CO_2 gas at 580°C for 4 h.

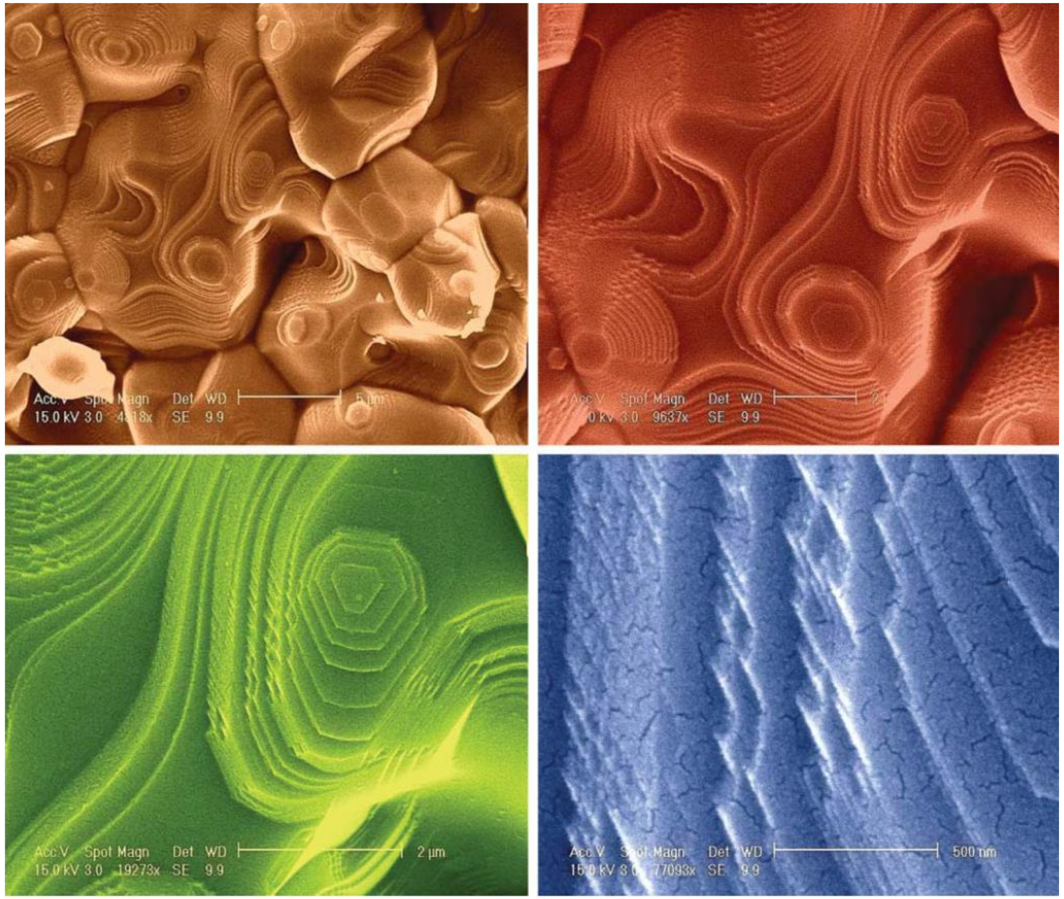
O_3
mite)

2 → Fuel or fuel precursors

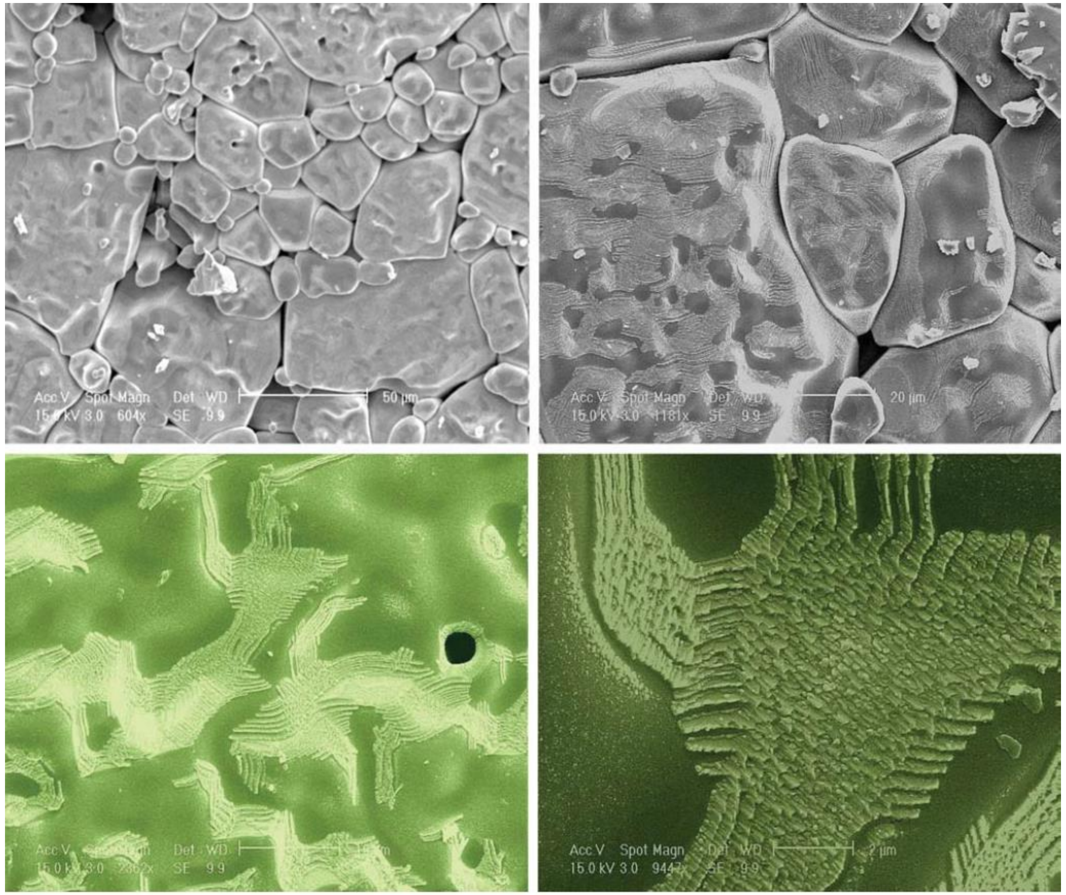
Microstructural attributes of electroceramics derived from CO_2-treated iron precursor

$$CO_2(g) + 2\ Fe_3O_4(magnetite, s) \xrightarrow{\geq 580^\circ C,\ 4h} 3\ Fe_2O_3(maghemite, s) + CO(g)$$

$$Fe_2O_3(maghemite, s) + MO\ (s) \xrightarrow{900^\circ C,\ 2h} MFe_2O_4\ (s); (M = Co, Ni, Zn)$$



SEM images of the sintered maghemite-derived $NiFe_2O_4$.



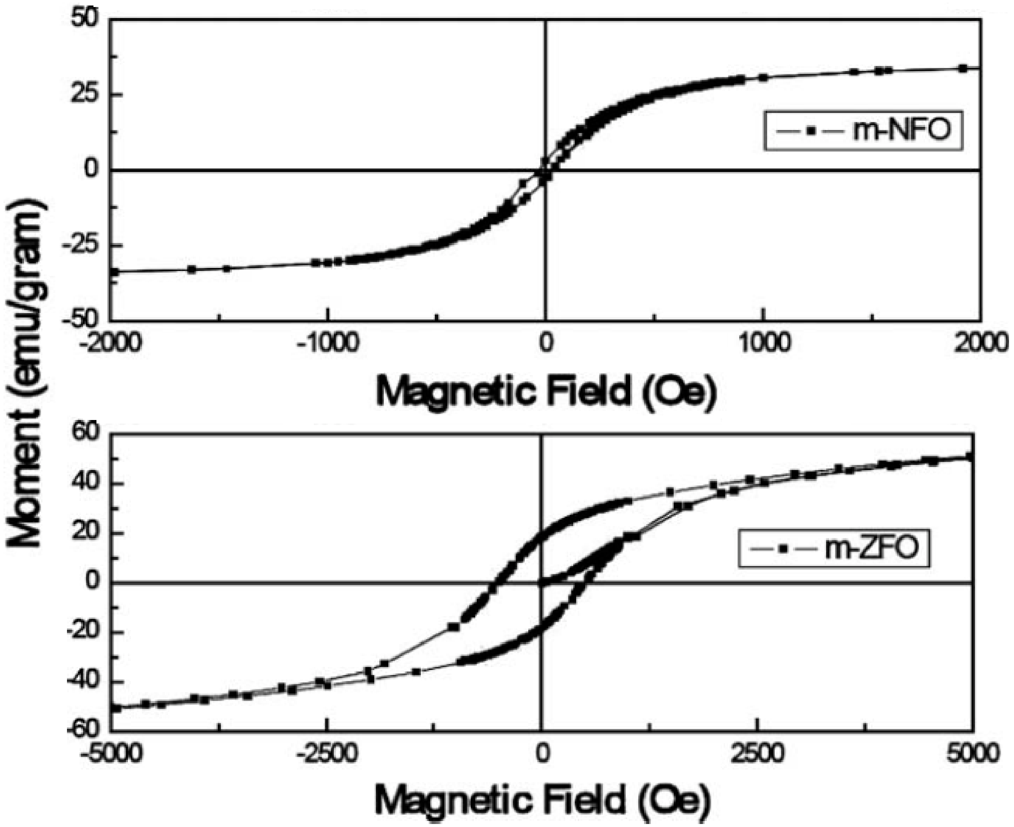
SEM images of the sintered maghemite-derived $ZnFe_2O_4$.

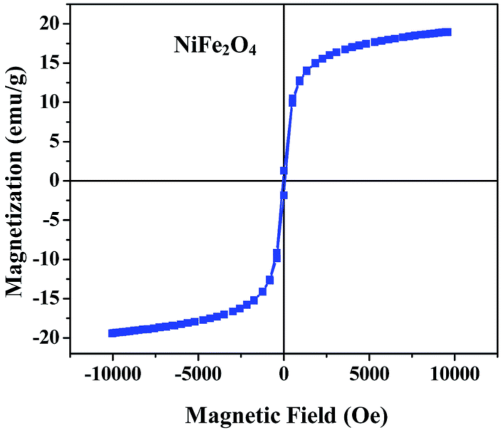
Magnetic attributes of electroceramics derived from CO_2-treated iron precursor

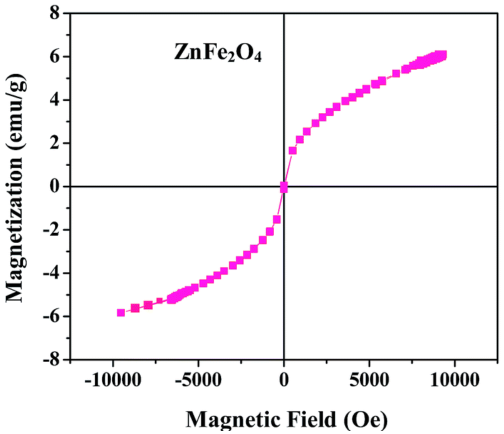
$$Fe_3O_4(magnetite, s) \xrightarrow{580℃,\, CO_2} Fe_2O_3(maghemite, s) + NiO\ (s) \xrightarrow{900℃,\, 2h} NiFe_2O_4\ (s) \qquad \boldsymbol{NFO}$$

$$Fe_3O_4(magnetite, s) \xrightarrow{580℃,\, CO_2} Fe_2O_3(maghemite, s) + ZnO\ (s) \xrightarrow{900℃,\, 2h} ZnFe_2O_4\ (s) \qquad \boldsymbol{ZFO}$$

M-H curves for the ferrites derived from post-CO_2 treated iron oxide (maghemite)







Other possibilities

I: Hydrogenation of CO_2 on Martian ilmenite/silicates*

$$CO_2(g) + 3H_2(g) \xrightarrow{M/TiO_2} CH_3OH + H_2O$$

$$\xrightarrow{M/FeTiO_3} CH_3OH + H_2O$$

$$(\Delta H_{298K} = -49.5\ kJ\ mol^{-1})$$

$$\xrightarrow{M/silicate} CH_3OH + H_2O$$

$$\xrightarrow{FeTiO_3/silicate} CH_3OH + H_2O$$

* M:

Cu, Zn (brought from earth) or Fe (brought from earth or extracted from ilmenite)

silicate:

- Anorthosite (plagioclase feldspar): $Ca(Al_2Si_2O_8)$
- Pyroxene: $(Ca^{2+}, Fe^{2+}, Mg^{2+})(Al^{3+}, Fe^{3+})(Si, Al)_2O_6$
- Olivine: $(Mg^{2+}, Fe^{2+})_2SiO_4$
- Or their mixture(s)

Most effective hydrogenation catalyst known:

- $Cu\text{-}Zn/ZrO_2$ (250-270°C)

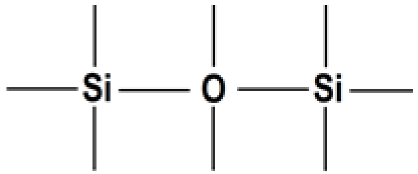
Why methanol?

- Liquid (bp: 64.7°C/1 atm.): potential candidate for DMFC-powered portable devices.
- Valuable intermediate in the production of **formaldehyde**, **methyl *tert*-butyl ether (MTEB)** and **acetic acid**.
- Global production: 40 million tons/y.

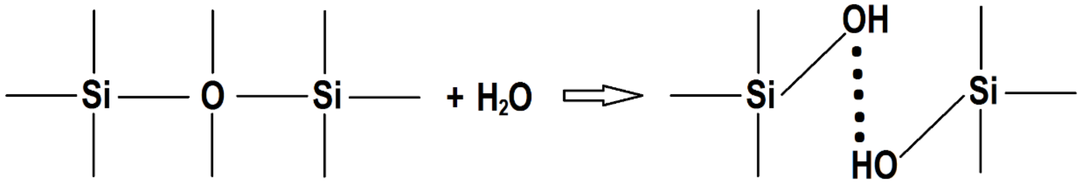
Other possibilities

II: High tensile strength lunar/Martian glass

Inherent strength of silicates comes from strong network-forming Si-O covalent bonds.



Presence of water causes hydrolysis of the Si-O bonds at the crack-tips and/or dislocations, and weakens the structure.



Hydrogen-bond bridges are an order of magnitude weaker than the Si-O bonds.

Rationale: Due to non-existence of water on moon and in the deep vacuum of free space, *hydrolytic weakening mechanism* of Si-O bonds is virtually absent.

True for Mars *also* (as there is not much free water in the atmosphere or on the ground).

→ imparts 'anhydrous strengthening' to the lunar-derived structural materials such as the 'lunar glass'.

→ Validates the speculation that tensile strength of lunar glass would be quite high compared to that on earth.

III. High tensile strength structures from regolith

- Silicates can be melted in a solar furnace and cast or drawn.
- Properties of silicate glasses on the Moon, Mars and in space different from those on earth.
- Permits the utilization of lunar and Martian resources in various space engineering applications.

- CMCs offer special advantages in certain niche applications.
- For example, large structures such as antennas and SPS supports are sensitive to potentially enormous thermal strains associated with periodic eclipses.
- Extremely low CTE Ti-silicate (as compared to common structural metals) could be used advantageously.

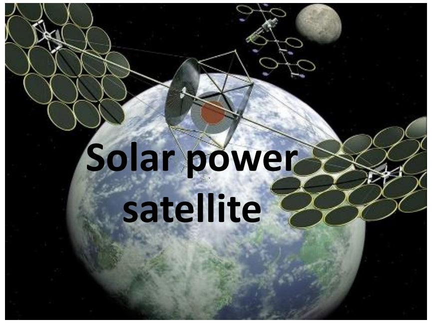
- Lunar/Martian glass (LG/MG) could potentially replace the conventional metal structures.
- LG/MG attractive and competitive (if not superior to) with metals derived from in situ resources by far more elaborate efforts.

- Similarly, the negative CTE of graphite fiber can be used to produce near zero CTE composites: Most suited for wide ranging temperature fluctuation experienced by the lunar surface each day.

- LG in the form of glass fibers is well-suited in many tensile stress situations: *fiberglass cloth, multiplied stranded cords & cables enable their use in lunar base and large space structures such as solar power satellites (SPS).*

- Thanks to the absence of any atmosphere/oxygen, fabrication of MMCs and CMCs on moon is not subject to the risk of oxidation and subsequent deterioration.

- Bulkheads for a habitat or beams/columns in an SPS are subject to flexural, compressive or mixed loading.
- Composite fiberglass would be advantageous:
  metal matrix composites (MMCs) and
  ceramic matrix composites (CMCs) are obvious choices.



Other challenges to building habitats: Tools for excavation and drilling

Ultrahigh vacuum on moon and lo-pressure CO_2-rich atmosphere on Mars with wide temperature ranges: severely restrictive working environment.

Even simplest exploration/mining operations in lo-gravity, gas-free, high-vacuum lunar environment become mammoth task and significantly impede the habitat building.

Moon/Mars surfaces also abound in fine dust: a potentially serious problem for the excavation and building equipment.

Lack of adequate power supply would restrict the tool dimensions as well as the hours of operation.

Almost non-existent literature on the failure mechanisms of drilling/cutting tools in a lo-pressure, lo-gravity, extremely dry environment.

Intended drilling/cutting tool(s) would have a combination of <u>high</u> Young's modulus, <u>high</u> fracture toughness and <u>high</u> Knoop hardness.

Boron carbide (B_4C) is the hardest material – second to diamond. Other carbides (such as silicon carbide, tungsten carbide, tantalum carbide, titanium carbide, chrome carbide), nitrides and carbonitrides, do possess a combination of these characteristics.

Though oxidation-mediated corrosion is not a concern on moon or Mars, adequate strength and impact fracture resistance are sought.

Path Forward

1. Fabricate structural and functional components (Table in slide 12) from precursors mimicking the lunar and Martian regolith simulants.
2. Evaluate the optical, electrical, structural and radiation-resistant properties of the components made in (1).
3. Assess and compare the tensile and compressive strength of lunar glass (LG, made by solar melting) and its composites in extremely dry (and slightly) humid environments.
4. Evaluate the propensity of hydrogenating CO_2 into methanol on titania-, ilmenite- and silicate-supported Fe-catalysts.
5. Explore the manufacturability of the structural and functional components by 3-D printing.
6. Validate the generation of H_2 and CO from Fe-concentrated regolith simulants and, CO_2 and H_2O.
7. Validate the performance of SOFC running on H_2 and CO derived in (6).
8. Seek funding from NASA/NSF/DOE for these new (and other regolith-related) activities.

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Thank you!

Supplemental slides

O_2, C and Fe via electrolysis in Li_2CO_3/Li_2O melt (~750°C)

$CO_2(g) + Li_2O(dissolved) \rightarrow Li_2CO_3(l)$

$Li_2CO_3(l) \rightarrow C(s) + Li_2O(dissolved) + O_2(g)$

Net reaction: $CO_2(g) \rightarrow C(s) + O_2(g)$

Making Fe from Fe_2O_3 WITHOUT CO_2:

$Fe_2O_3(s) + Li_2O\ (dissolved) \rightarrow 2\ LiFeO_2\ (l)$ (1)

Molten salt electrolysis of lithium ferrite forms elemental iron, liberating Li_2O:

$2LiFeO_2(l) \rightarrow 2Fe(s) + Li_2O\ (dissloved) + \frac{3}{2}O_2(g)$ (2)

Liberated Li_2O provides a path for continued dissolution of Fe_2O_3. Fe forms via combination of (1) and (2), ***without*** CO_2:

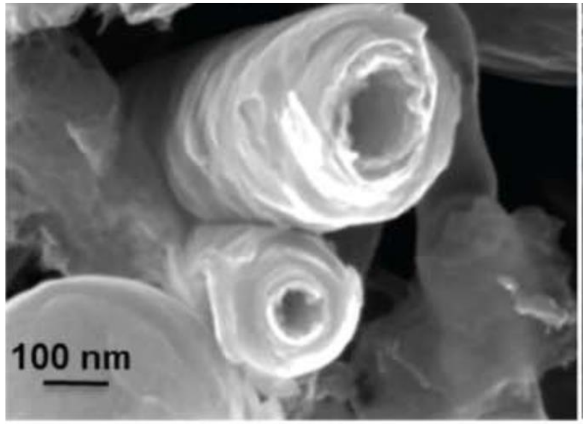
$Fe_2O_3(s) \rightarrow 2\ Fe(s) + \frac{3}{2}O_2(g)$ (3)

Fe/Fe$_C$ and CNF/CNT via electrolysis in Li_2CO_3/Li_2O melt (~750°C)

Making Fe or $Fe_{(C,\ diss.)}$ from Fe_2O_3 + CO_2:

$$Fe_2O_3(s) + CO_2(g) \rightarrow 2\ Fe\ (s) + \boldsymbol{C}(s) + \tfrac{5}{2}O_2(g)$$

Or, $Fe_2O_3(s) + CO_2(g) \rightarrow 2\ Fe_{(C,dis.)}\ (s) + \tfrac{5}{2}O_2(g)$



MWCNT

Fe or $Fe_{(C,\ diss.)}$ from Fe_3O_4 + CO_2:

$$Fe_3O_4(s) + CO_2(g) \rightarrow 3\ Fe\ (s) + \boldsymbol{C}(s) + 3\ O_2(g)$$

Or, $Fe_3O_4(s) + CO_2(g) \rightarrow 3\ Fe_{(C,dis.)}\ (s) + 3\ O_2(g)$

Alternatively, in the case of Fe_3O_4 + CO_2:

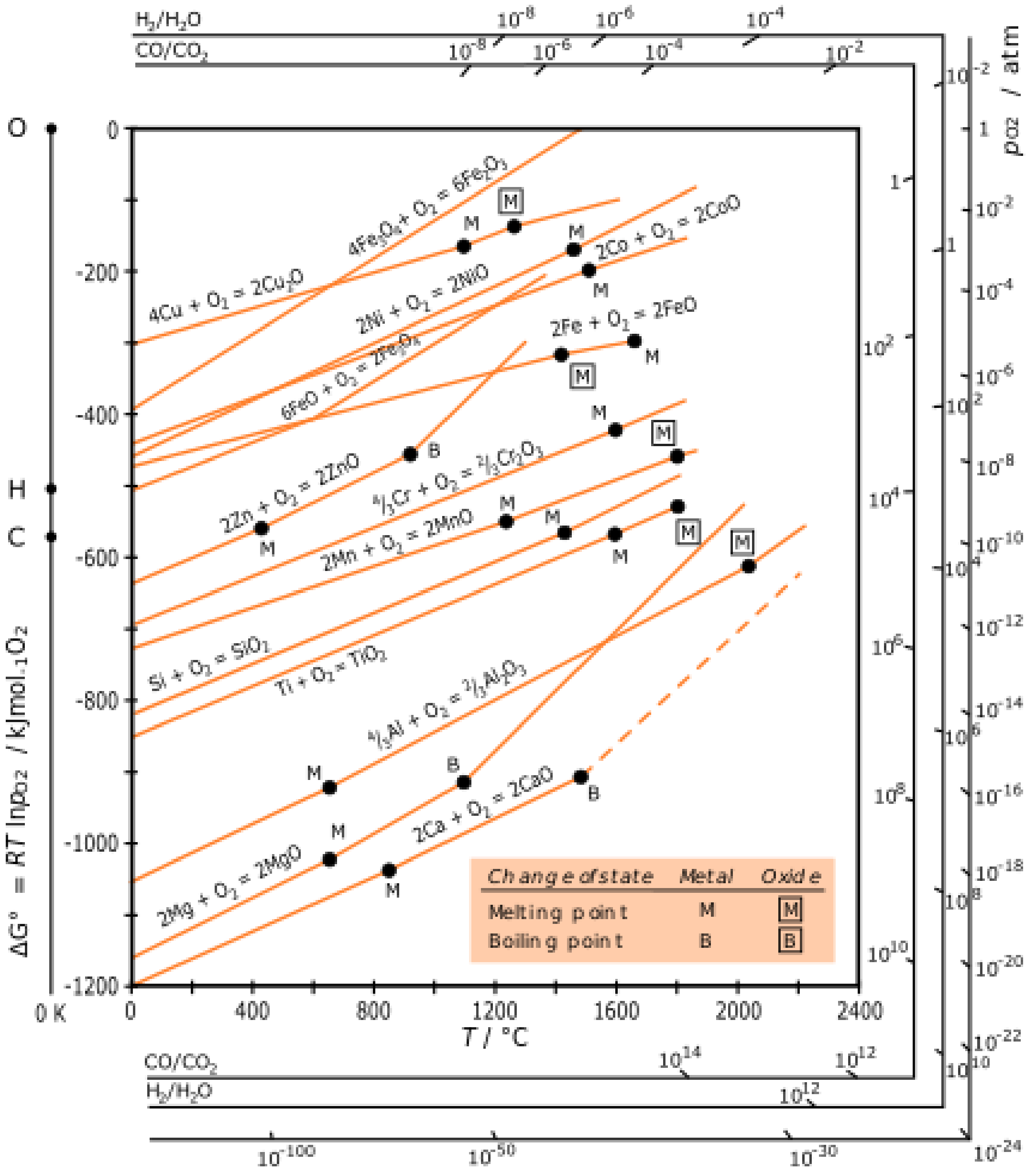
$$2Fe_3O_4(s) + CO_2(g) \rightarrow 3Fe_2O_3(s) + CO(g)$$

$$Fe_2O_3(s) + CO_2(g) \rightarrow 2\ Fe\ (s) + \boldsymbol{C}(s) + \tfrac{5}{2}O_2(g)$$

Or, $Fe_2O_3(s) + CO_2(g) \rightarrow 2\ Fe_{(C,dis.)}\ (s) + \tfrac{5}{2}O_2(g)$

$$\Delta G = -nFE \qquad \left(F = 96.487\frac{kJ}{V}; n = 4\right)$$

Oxide stability increases



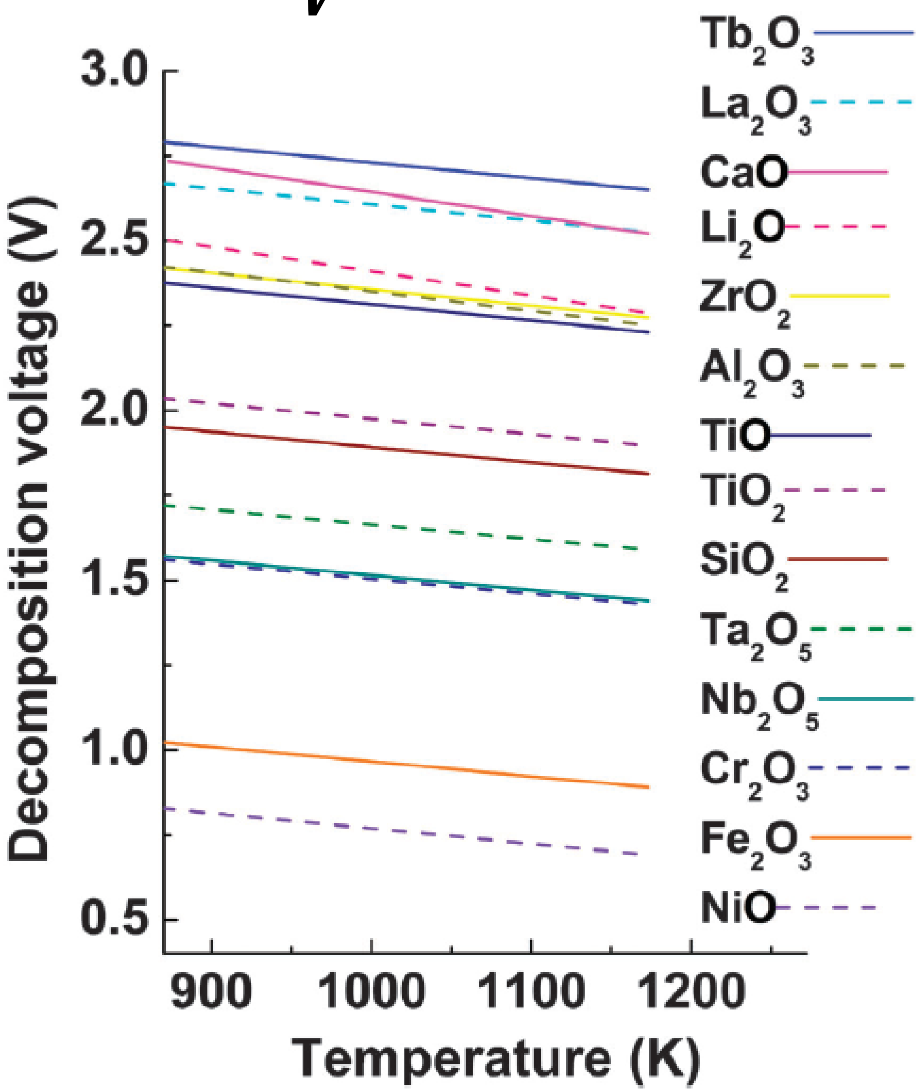


Fig. 1 The decomposition voltages of typical solid oxides, calculated based on the corresponding Gibbs free energy changes derived from HSC Chemistry version 6.

Oxide stability increases

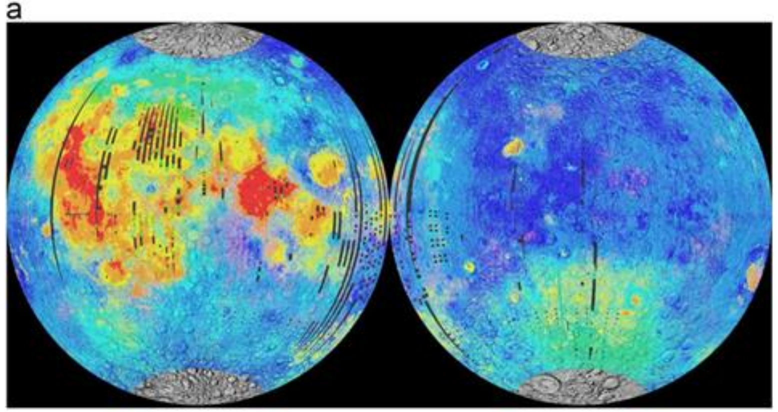


Fig. 1. (a) Distribution of rock types on the nearside (left) and the farside (right) of the Moon. Blue: anorthositic highlands; yellow: low-Ti basalts; red: high-Ti basalts. The large yellow/greenish area in the southern hemisphere of the farside is the South Pole-Aitken Basin, and the colours mostly reflect the more Fe-rich nature of the lower crust exposed by the basin rather than basaltic material (Spudis et al., 2002; image courtesy of Paul Spudis).

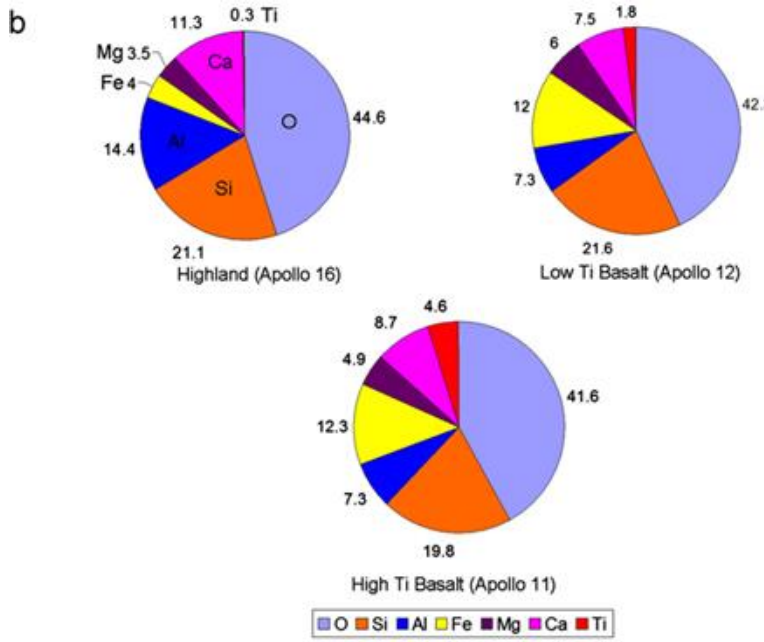


Fig. 1. (b) Chemical compositions of lunar highland minerals (Apollo 16), low-Ti basalts (Apollo 12), and high-Ti basalts (Apollo 11). (Diagrams based on data from Stoeser et al. (2010)).

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The production of oxygen and metal from lunar regolith

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Table 1
Chemical compositions of lunar simulants JSC-1 (NASA, 2005) and NU LHT (NASA, 2008). Composition ranges are given for JSC-1 to reflect the slightly varying specifications for this material.

Oxide	JSC-1, % by mass	NU LHT, % by mass
SiO_2	46–49	46.7
Al_2O_3	14.5–15.5	24.4
CaO	10–11	13.6
MgO	8.5–9.5	7.9
Na_2O	2.5–3	1.26
K_2O	0.75–0.85	0.08
TiO_2	1–2	0.41
MnO	0.15–0.20	0.07
FeO	3–4	–
Fe_2O_3	7–7.5	4.16
Cr_2O_3	0.02–0.06	–
P_2O_5	0.6–0.7	0.15

Envisaged **on-Mars** usage of SiO_2, Al_2O_3, Fe_2O_3, Fe_3O_4, H_2O, CO_2, {CaO, MgO and TiO_2}

Material(s)	Application(s)
SiO_2, Al_2O_3, FeO_x (with/without alkali metal & phosphate microconstituent incorporation)	Aluminosilicate/ferro aluminosilicate as (a) structural ceramics (b) reinforcement fiber glass (c) radiation-shielding glass (d) habitat windows
MgO, CaO (calcined dolomite)	Flux in iron and steel making
CaO, SiO_2 (calcium silicate)	**Cal-Sil** - a low cost structural material (safe alternative to **asbestos**) used in bricks, roof tiles, roads, insulation, etc. Ca_2SiO_4 (2CaO.SiO_2) a cement-compatible spacer
MgO, SiO_2 (magnesium silicate)	Steatite - a low cost material with • high electrical resistance at high temperatures • good mechanical strength • very low dielectric loss factor. • Ideal for high frequency, low loss, and high voltage insulation.
FeO_x, TiO_2 (iron titanate, ilmenite) CaO, TiO_2 (calcium titanate) MgO, TiO_2 (magnesium titanate)	Pure and doped $FeTiO_3$, solid-state oxygen carrier and fuel oxidation catalyst In doped form, $CaTiO_3$ is a solid-state oxygen carrier and fuel oxidation catalyst $MgTiO_3$ useful as low dielectric support material for making on-chip capacitors, high frequency capacitors and temperature compensating capacitors
Fe_2O_3, Fe_3O_4, H_2O and CO_2	Precursors to O_2 generation and fuel manufacturing
Fe_2O_3, Fe_3O_4, H_2O and CO_2	Precursors for the fabrication of ceramic permanent magnet (motors, actuators)

Goals:

Maximized ISRU
Lo earth-dependence
Lo energy usage
Simple processing
High-end products